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(54) Title: CATALYTIC CELLULIGNIN FUEL

(57) Abstract: The present invention relates to a catalytic cellulignin fuel obtained by a biomass pre-hydrolysis process and that is composed of cellulose and globulized lignin with a specific surface of about 1.5 - 2.5 m²/g. The cellulignin fuel according to the invention may be ground down to particles smaller than 250 µm and has a combustion heat value that can reach up to 18 - 20 MJ/kg and an ignition time equal to or shorter than 20 ms (0.02s).

11/p.1b

Title: "CATALYTIC CELLULIGNIN FUEL"**Field of the Invention**

The present invention relates to a new fuel obtained from biomass.

Background of the Invention

5 The energy obtained from biomass is highly positive from the point of view of energy. For instance, the energetic efficiency of the so-called short-rotation biomass is 89.5%, and the rate of liquid energy is 9.48 times higher. However, in spite of this fantastic energetic efficiency, biomass cannot compete with fossil fuels due to the high costs resulting from the large number of steps required to produce it
10 and also due to the difficulty in handling the raw biomass, which renders it not very practical.

 The following points related to the process for producing biomass should be taken into account: 1) planting and cultivation (propagation); 2) expenses with nutrients (fertilization); 3) exposure to the sun; 4) temperature; 5) precipitation; 6)
15 conditions of soil and water; 7) harvesting method; 8) resistance to diseases; 9) competition in the area with production of foodstuffs, pastures and fibers; 10) area availability; 11) transport of the raw biomass.

 Biomasses are composed of cellulose, hemicellulose and lignin, the composition being exemplified in Table 1, and microstructure according to figure 1.

Table 1

Cellular wall	Typical Composition - Pine Tree (%)		
	hemicellulose	cellulose	lignin
LM - middle lamella	-	-	3.0
P - primary wall	1,4	0,7	8,4
S - secondary wall			
S1	3,7	6,13	10,5
S2	18,4	2,7	9,1
S3	5,2	0,8	
Total	28,7	40,3	31,8

The cellular walls are composed of macrofibrillae, microfibrillae, micellae and cellulose molecules. The nuclei of the cells (cytoplasm) is composed of aqueous solutions. The following formulas represent the approximate estimates of the specific surface (area per unit of mass) of the biomass in the hypothesis of its microstructure being completely released.

1- Geometry with a Square section and length l (S and M: cell surface and cell mass).

$$S = 4bl; M = 4ble\rho \therefore \frac{S}{M} = \frac{4bl}{4ble\rho} = \frac{1}{e\rho}$$

10

broadness of the cell $b = 10\mu\text{m}$

thickness of the cell wall: $e = 1.0\mu\text{m}$

$\rho = 1.5 \text{ g/cm}^3$

$= 1.5 \times 10^6 \text{ g/m}^3$

15

2. Specific area of the macrofibrillae, microfibrilla, miscellae and cellulose molecules.

$$S = \pi \phi l; M = \frac{\pi \phi^2}{4} l \rho \therefore \frac{S}{M} = \frac{\pi \phi l}{\frac{\pi \phi^2}{4} l \rho} = \frac{4}{\phi \rho}$$

2.a - Specific area of the macrofibrilla ($\phi = 50\text{nm}$; Macropores $>50\text{nm}$)

$$\frac{S}{M} = \frac{4}{50 \times 10^{-9} \times 1,5 \times 10^6} = 53 \text{m}^2 / \text{g}$$

2.b - Specific area of the microfibrillae ($\phi = 50/4 = 12,5\text{nm}$; Mesopores 2nm

5 $<\phi < 50\text{nm}$)

$$\frac{S}{M} = \frac{4}{12,5 \times 10^{-9} \times 1,5 \times 10^6} = 213 \text{m}^2 / \text{g}$$

2.c - Specific area of the miscella ($\phi = (12,5/4)\text{nm} = 3,1\text{nm}$; Micropores $\phi < 2,0\text{nm}$)

$$\frac{S}{M} = \frac{4}{3,1 \times 10^{-9} \times 1,5 \times 10^6} = 860 \text{m}^2 / \text{g}$$

10

2.d - Specific area of the molecules of cellulose ($3,1/6\text{nm} = 0,517\text{nm}$)

$$\frac{S}{M} = \frac{1}{0,517 \times 10^{-9} \times 1,5 \times 10^6} = 1290 \text{m}^2 / \text{g}$$

$$N = 1 + 6 \sum_0^n n_i = 1, (1 + 6 = 7), (1 + 6 + 12 = 19), (1 + 6 + 12 + 18 = 37).$$

The theoretical specific area for the cell is of about $0.7\text{m}^2/\text{g}$, of about $50\text{m}^2/\text{g}$ for the macrofibrillae, of about $200\text{m}^2/\text{g}$ for the microfibrillae, of about $900\text{m}^2/\text{g}$ for the miscella, and of about $1300\text{m}^2/\text{g}$ for the molecules.

As far as solid fuels are concerned, their conventional combustion comprises 5 zones: first non-reactive solid zone (heating and drying), second reaction zone of condensed phase (solid pyrolysis), third reaction zone of gaseous phase (pyrolysis of gaseous phase and oxidation), fourth primary combustion zone (gaseous phase), fifth post-flame reaction zone (secondary combustion). The specific kinetics and reactions of each zone is not completely known yet.

20

Figure 2 illustrates the conceptual model of conventional combustion for wood. Wood is anisotropic and hygroscopic, and its fibers (tracheids) are hollow and have a length of from 3.5 to 7.0mm in soft wood, and from 1 to 2 mm in hard wood. The linked water is of about 23%, and the total moisture reaches 75%. Cellulose, hemicellulose and lignin behave as polyalcohols wherein the main functional group is the OH group. Cellulose is a linear polysaccharide of anhydrous glucose with 1 \rightarrow 4- β glucoside bonds. After oxidation, the functional groups are carbonylic, ketone and carboxylic groups. On the other hand, hemicellulose is a polysaccharide with branched chain, the main components of which are 4-O-methylglucoroxylanes in hard wood and glucomanes in soft wood. The main functional groups thereof are carboxylic, methylic and hydroxylic groups. Lignin, on the other hand, is a tridimensional backbone of 4 or more substituted phenylpropane units. The basic constitutive blocks are guayaquil alcohols (soft wood) and seringyl alcohol (for the two types of wood), and the dominant bonds are β -O-4.

The structures of cellulose and lignin are highly oxygenated and the location of the functional groups is useful in understanding the mechanisms of pyrolysis and oxidation.

For the purpose of comparison, it is observed that the structure of the mineral coal is aromatic, it has few hydroxylic functional groups and β -O-4 bonds. Nitrogen and sulfur are part of the structural rings with little nitrogen existing in the amine form. The fact that the oxygen content is very low in coals when compared with wood is highly significant, since it imparts greater reactivity to the latter.

In the conventional combustion of wood the drying stage involves, in fact, 4 steps, namely 1) energy required for heating the wood up to 100° C (373°K) = $0.08 \times 100 \times (1 - TU)$ kJ/kg, wherein TU is the moisture content (percentage); 2) energy required for heating water = 4.2×100 kJ/kg; 3) energy required for vaporizing the water = 2.26 MJ/kg; and 4) energy required for releasing the linked water $15.5 \times TU$ kJ/kg (average). The predominant value is the energy from vaporization of water.

The heating stage comprises three factors that have significant influence: the first one is the energy for heating up to the pyrolysis temperature (500 - 625 °K); the wood specific heat is 1113 J/g at 273 ° K and 1598 J/g at 373 °K, while the specific heat of the wood with 35% of moisture is 2.343 J/g at 300 °K. Secondly, there is the influence of the moisture preventing the particle core be heated up to the tem-

perature at which water is evaporated and establishing the reaction states. The third factor of influence is the moisture in the increase of the thermal conductivity of the wood particle, which may at most double its value. In addition to its influence on the drying and heating, moisture also causes significant effects on the solid state pyrolysis.

The next stage is the solid pyrolysis step. In this combustion zone, reactions of cleavage of the molecules into gaseous fragment and condensation reactions prevail, whereby coal is produced (tar resulting into 3 final fractions: a gaseous one, a liquid one, and a solid one - coal). The pyrolysis temperatures are: hemicellulose (500 - 600 ° K), cellulose (600 - 650 ° K) and lignin (500 - 773 K). Table 2 shows the pyrolysis products from cellulose and xylan, with a high tar content that causes a secondary combustion close to the oils for the wood.

Table 2: Pyrolysis Products from Cellulose (873 °K) and Xylan (773 °K)

Product	Cellulose (% P)	Xylan (% P)
Acetaldehyde	1,5	2,4
Acetone Propinaldehyde	0,0	0,3
Furanics	0,7	Tr
Propenol	0,8	0,0
Methanol	1,1	1,3
2-Methylfuran	Tr	0,0
2,3-Butanedione	2,0	Tr
1-Hydroxy-2-Propan glycoxal	2,8	0,4
Acetic acid	1,0	1,5
2-Furaldehyde	1,3	4,5
5-Methyl-2-Furaldehyde	0,5	0,0
CO ₂	6,0	8,0
H ₂ O	11,0	7,0
Coal	5,0	10,0
Tar	66,0	64,0

Tr = trace

The opening of aromatic rings is an intermediate step in forming the volatile material, generating acetic acid and acetaldehyde, which are decomposed by decarboxylation of acetic acid ($\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$) and decarbonilation of the

acetaldehyde ($\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$). From the hemicellulose, the resulting product is C_2H_4 and CO from the propanol. In the next zones, there will be sequence in the pyrolysis and oxidation, giving CH_4 , C_2H_4 , CO and CO_2 as final products.

The pyrolysis of lignin is different in comparison with the hemicellulose and cellulose and at 823 K it produces the following components: coal (55%), gaseous fraction (45%) composed of CO (50%) CH_4 (38%), CO_2 10%) and C_2H_6 (2%). The tar is composed of phenylacetylene, anthracene and naphthalene. Table 3 shows the formation of coal in the pyrolysis of several different materials.

Table 3: Coal Formation in the Pyrolysis of Several Different Materials

10 (673K)

Material	Coal (%P)
Cellulose	14,9
Poplar (wood)	21,7
Larch (wood)	26,7
Aspen (branches)	37,8
Douglas (bark)	47,1
Klason Lignin	59,0

Moisture also has a considerable influence on the particle pyrolysis since it causes an enormous difference in temperature between the particle core and the periphery thereof (400 °K), creating a physical separation between the heating and drying zone and the pyrolysis zone. The dominant influence of moisture is to reduce the flame temperature of the burner, directing the product to coal formation and reducing the rate of pyrolysis. The theoretical flame temperature of the wood combustion is given by:

$$T_a = 1920 - (1,51[TU/(1-TU)] \times 100) - 5,15 X_{\text{exAr}}$$

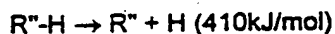
20 wherein T_a (K) is the adiabatic flame temperature, TU is the fraction of the moisture contents, and X_{exAr} is the percentage of air excess. In addition to the

reduction of the adiabatic temperature, there is an increase in the air excess, given by:

$$X_{\text{exar}}(\%) = 40[TU/(1-TU)]$$

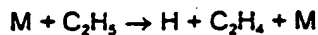
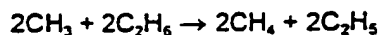
For $TU > 33\%$, $T_s = 1740^\circ\text{K}$ and for $TU = 50\%$, $T_s = 1560^\circ\text{K}$ and consequently there is a decrease in the volatile content and an increase in the coal content. Finally, one should cite that the ashes reduce the local temperature and catalyze the formation of coal.

Next, the pre-combustion reaction occurs, which represent the cleavage of volatile material into fragments of radicals dominated by reactions of initiation of chains of the type:



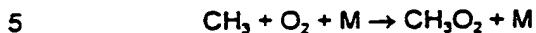
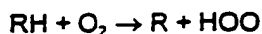
wherein $R = C_2H_6, CH_3$, etc. e $R'' =$ methylic group.

In wood, the first reaction is most probable due to its lower energy, and an example thereof is given below:



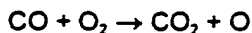
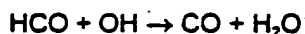
wherein M is a heat (ash or vapor)-removing particle or molecule. If R'' contains two or more carbon atoms, the C-C bond is broken preferably instead of the C-H bond. In addition to the reactions of chain initiation, the pre-combustion zone includes reduction reactions with recombinations of radicals $R + R' \rightarrow R-R'$, especially if the pre-combustion zone is spatially broad. An example thereof is the recombination of nitrogen forming N_2 instead of NO_x .

After the pre-combustion reactions, primary combustion reactions occur. Oxygen and fuel mixed in the primary combustion zone results in a number of reactions of free radical, producing CO_2 and H_2O .



HCO and CO ($\text{CH}_2\text{O} + (1/2)\text{O}_2 \rightarrow \text{HCO} + \text{OH}$ or $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO} + 2\text{HO}$) are formed from CH_2O , and their concentration is maximized at flame temperatures of 1320K, which is the wood combustion temperature.

10 Finally, the post-combustion reactions occur: the processes of wood combustion occur at low temperature, and reactions of chain end occur in the secondary combustion. The hydroxyl radical (CH_2O) is of great significance when it is present at high concentrations. The main end reactions are:



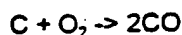
the latter being of lesser importance in this zone. The CO_2 production from CO is controlled by the OH concentration, which is relatively high for low temperature systems (wood). It follows that the chain end is the recombination of H and OH groups aided by heat-removing species (M). The $\text{C}:\text{H}$ ratio is relatively high for soft wood (1:1.45) and hard wood (1:1.37) compared with mineral coals (1:0.17). The wood solid pyrolysis produces water, CH_4 , C_2H_4 , and C_2H_6 , resulting in a substantial amount of hydrogen in the volatile gases to increase the concentration of hydroxyl radical for a complete and rapid oxidation (greater reactivity). There is no complete expressions in the literature for this system, due to the large number of variables associated to the oxidation of the wood volatiles.

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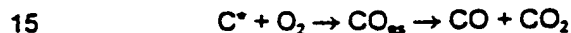
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In the combustion of (wood) charcoal, the charcoal obtained from the pyrolysis is porous and contains various free radicals for O_2 attack. In addition, it con-

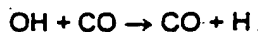
contains oxygen and hydrogen, its empirical chemical formula being $C_6.7H_{3.3}O$. Three mechanisms were proposed for the charcoal oxidation, it being recognized that the combustion rate is limited by the sites of free radicals on its surface. The charcoal oxidation is also limited by the mass transport. The first mechanism is the Boudouard, as the general indicator of charcoal combustion.



This reaction is highly endothermic with the following reaction constants: 1.1×10^{-2} (800°K) and 57.1 (1200°). The CO released is volatile and its combustion is completed in the flame out of the particle. The second mechanism is the chemical adsorption of O_2 directly on the coal. The activation energy of the O_2 adsorption on the porous surface of the coal ranges from 54 kJ/mole to 105 kJ/mol, respectively, for chemically adsorbed quantities from zero to 2.5 moles of O_2 per gram of coal. The chemical adsorption reactions are:



The asterisk indicates an active site of reaction, m stands for moveable species, and es stands for stable species. The charcoal active sites can be generated by the mechanism of pyrolysis. The third mechanism of charcoal oxidation involves reactions of hydroxyl radicals in the active sites given by:



Hydroxyl radicals are internally generated by homolytic cleavage of the various hydroxylic functional groups existing in the wood or dissociation of the moisture released by the fuel. The moisture influence on the coal oxidation are not well known, as in the case of the pyrolysis of wood. It is speculated that the moisture "deletes" the sites, reducing the rate of coal oxidation. The presence of moisture delays the rate of oxidation of charcoal.

In short, the wood combustion is a multistage process that involves heating and drying, solid state pyrolysis, producing volatile compounds and coal, re-

actions of gaseous phases (pre-combustion, primary combustion and post-combustion) and combustion of the coal. The various functional groups existing in wood generate a significant number of volatile products from the solid pyrolysis of particles, the various functional groups and the high aliphatic contents increasing the reactivity of wood, contributing to the high proportion of flames in the combustion of the wood with respect to mineral coal. The moisture increases the thermal conductivity, results in greater production of coal in the solid state pyrolysis, increases the concentration of hydroxyl groups for the reactions of gaseous phase and of the coal, and reduces the oxidation rate of the coal, decreasing its temperature and "deleting" the reactive sites.

In view of the complexity and the operational disadvantages presented by the conventional combustion processes, it was desirable to develop a new fuel from biomass that could meet the essential requirements of combustion and overcome the technical drawbacks of the known fuels.

In this regard, various studies have been carried out for the development of new fuels from biomass and some attempts have already presented satisfactory results, as in the case of a cellulignin fuel mentioned in the article "Cellulignin: a new thermoelectric fuel" by Daltro G. Pinatti, Christian A. Vieira, José A. da Cruz and Rosa A. Conte, which relates to a product from generic cellulignin obtained by a process of pre-hydrolysis of biomass without optimized control. However, it was still desired to obtain a fuel that would present even more advantageous results, mainly from the economic point of view and the applications thereof in the main thermoelectric technologies: ovens, boilers, gas turbines and generation of energy by hydrodynamic magnet (MHD).

Therefore, the objective of the present invention is to provide a new cellulignin fuel with catalytic properties that will meet these market requirements with improved combustion characteristics.

Summary of the Invention

The present invention relates to a catalytic cellulignin fuel that is composed of cellulose and globulized lignin and that presents a specific surface of about 1.5 - 2.5 m²/g, with an average value of 2.0 m²/g.

Brief Description of the Drawings

- Figure 1 shows a schematic diagram of the biomass cellular structure.

5 -Figure 2 shows the steps of the conventional combustion process of solid fuels.

- Figures 3a - 3e show microphotographs of the structure of a cellulignin according to the present invention, while Figure 4 graphically shows diffractograms of X-rays for wood, cellulose and cellulignin.

10 Figure 5 shows a graphic of the enthalpy variation for the reactants in a process of catalytic combustion of coal, and Figure 6 shows ratio of the burning time of mineral coal to the particle size. Figures 7a and 7b in turn shows the power irradiated in the combustion of cellulignin according to the present invention.

Figures 8 - 12b illustrate systems and equipment useful for the combustion of the cellulignin fuel now defined.

15 Detailed Description of the Invention

After detailed studies, the inventors achieved a catalytic cellulignin fuel obtained from biomass, which allows a surprising result regarding its combustion. The catalytic cellulign fuel of the invention is prepared by a process of pre-hydrolysis of biomass using a reactor such as described in the Brazilian patent application filed
20 on this same date for "An Apparatus and Process of Pre-Hydrolysis of Biomass". The referred-to pre-hydrolysis may be carried out for any type of biomass, such as wood, sugar-cane bagasse and straw, vegetable residues, barks, grass, organic part of garbage, etc.

The pre-hydrolysis process described in the above-mentioned patent
25 application generically comprises steps of discharging the biomass in a helical feeder, in the device of pre-hydrolysis of biomass, followed by a pressurization operation comprising the following steps: 1) filling the device of pre-hydrolysis of biomass with a pre-heated acidic solution; 2) heating; and 3) pressurization, said process being distinguished by the fact that the pre-hydrolysis is carried out simultaneously with a rotary oscillation of the biomass pre-hydrolysis apparatus, purging of the
30 vapor and controlling the temperature, pressure, acid contents, pre-hydrolysis time,

and liquid/solid relationship, monitoring the sugar contents until a value of about 10 Bricks is reached by means of a sugar-measuring device. Then, the steps of discharge of the pre-hydrolyzate into a tank through a heat-exchanger, sugar-recovering washing; and discharge of the cellulignin into mechanical washers or carriages to be washed by percolation are carried out.

Again referring to figure 1 and Table 1 presented above, one can see that according to the processes of hydrolysis of biomass the cellulose fibers release is not complete, because the hemicellulose has its highest concentration in the second layer (S2) of its secondary wall. With the pre-hydrolysis process developed by the present inventors, it now has been achieved a product with a specific surface of about 1.5 - 2.52/g, with an average value of 2m²/g, measured by BET (Brunace, Emmett and Teller) and a slush number 100, this meaning that this pre-hydrolysis process reaches the level where partial release of the microfibrille occurs.

The confirmation of this microfibrillae release is illustrated in the microphotographs presented in figures 3a - 3e. Figure 3a shows the microstructure of the catalytic cellulignin according to the invention after pre-hydrolysis, with an increase of 1000 times (scale of 10µm). Figure 3b shows a cellular wall presenting the middle lamella with an increase of 10.000 times (scale 1µm), while figure 3c shows the cellular wall with an increase of 50.000 times (scale 100nm) and figure 3d shows the cellular wall with an increase of 100.000 (scale of 10µm). Figure 3e shows the microstructure of a second sample where it is possible to observe the lignin globulization.

The combination of an open structure, while maintaining the crystalline characteristics of cellulose demonstrated by X-rays diffraction, as can be seen in figure 4, enables one to achieve the following characteristics of the cellulignin fuel:

1 - due to the maintenance of the cellulose crystalline characteristics, it is possible to effect the grinding of the cellulignin according to the present invention down to below 200µm by using hammer mills without the need for intermediate sieving and with a low energy consumption (about 12kWh/t). Due to this characteristic, the new fuel is called "catalytic" lignin.

2 - Easy drying of the water in rotary dryers, ovens or cyclones: the cellulignin according to the invention, which has particle size below 200µm, presents a completely open structure which permits it to be dried at 500ppm of moisture and at low temperature, that is to say, at 125° C (temperature of chimney gas).

- 13 -

The water contained in biomass is one of the worst characteristics for combustion. and the drying achieved for the cellulignin of the invention allows the obtention of a value of $18^{\circ} 20\text{MJ/kg}$ for the combustion heat, which is the double of the combustion heat of biomass with normal moisture of 45%.

5 Therefore, one of the great technical advantages obtained by the present invention is that the catalytic cellulignin may be externally dried with the heat of the chimney gas and subsequently burned in dry form. This option is unfeasible for raw wood.

3 - When in the powder form, the cellulignin density is of 600kg/m^3 in the so-called accommodated form, and 450kg/m^3 in the non-accommodated form. This represents an average energetic density of $20\text{MJ/kg} \times 500\text{kg/m}^3 = 104\text{MJ/m}^3$, compared with the energetic density of $40\text{MJ/kg} \times 800\text{kg/m}^3 = 3.2 \times 10^4\text{MJ/m}^3$ for fuel oils, which means that the tanking and handling of the catalytic cellulignin fuel are only three times as high as those of fuel oils, and it is drastically easier than the handling of raw biomasses (wood and vegetable residues), which require large volumes and huge equipment.

4 - The dosage of the cellulignin of the invention in combustion apparatus is made, for instance, by means of helical dosing device or rotary valves and the feeding of air such as drag-gas air in the proportion of air:cellulignin of about 3.28:1 by weight and 1261.6:1 by volume. This imparts to the cellulignin a characteristic equal to that of the gases or liquids in the operations of dosing and feeding, providing a drastically easier operation than the conventional dosing and feeding of solid fuels, especially biomasses.

5 - The microstructures pictures show the disclosure of the microfibrillae in a dimension of 50nm . This technique establishes the correlation between the process (hemicellulose digestion) and the product (open structure with medium specific surface). It constitutes one of the main new characteristics of the product, as well as the technology of controlling the pre-hydrolysis process in the production of the catalytic cellulignin fuel.

30 6 - Table 4a illustrates the physical characteristics of the Micropores (Active Sites) and table 4b presents the distribution of the Meso and Macropores. The former was determined by BET - Adsorption of N_2 and the latter was determined by

Hg porosimetry. The total specific area measured by BET is about 2.20m²/g, and the specific area of the macro and meso pores were the larger portion of the total area. The calculation thereof from the average radius of the pore measured by Hg porosimetry results in 1.80m²/g, admitting a cylindrical symmetry of the pore ($l = 2r$). This conclusion is coherent with the low micropores volume (1.1x10⁻³cm³/g) measured by BET. The distribution of the macro and meso pores has its maximum value ranging from 1 to 5µm (1000 - 5000nm), this size coinciding with the voids of the cells photographed by MEV (figures 3a, 3b, and 3e). The data of table 4 and the microstructures of MEV permit the complete characterization of the catalytic cellulignin fuel according to the present invention. The micropores are measured by the iodine number equal to 100; in the case of the catalytic cellulignin still there is no instrumentation that enables one to appraise the of the micropores (2nm) contribution in the combustion.

Table 4a: Physical characterization of the Micropores

(Active Sites - $\phi < 2.0$ nm)

Samples	Crystalline density ⁽¹⁾ (g/cm ³)	Specific area ⁽²⁾ (m ² /g)	Micropore Radius ⁽²⁾ (nm)	Micropore volume ⁽²⁾ (x10 ⁻³ cm ³ /g)
1- Wood	1,284	0,459	0,948	0,217
2 - Cellulignin without grinding - pre-hydrolysis time	1,331	0,756	0,980	0,371
2a - 0,5h (oscilation)	1,337	1,463	0,905	0,662
2b - 1,0h (oscilation)	1,334	1,342	0,970	0,651
2c - 1,0h (static)	1,351	2,249	0,964	1,080
2d - 2,0h (oscilation)				
3-Grinding effect				
3a-cellulignin without grinding	1,252	2,483	1,197	1,496
	1,353	2,758	0,997	1,375
3b- 297µm< ϕ <354µm	1,368	2,013	1,135	1,143
3c- 177µm< ϕ <210µm	1,375	2,114	1,032	1,090
3d- 125µm< ϕ <149µm	1,372	1,915	0,962	0,921
3e- 88µm< ϕ <105µm	1,346	3,179	0,914	1,454

3f- $\phi < 74 \mu\text{m}$				
4- Wood and carbonized Cellulignin				
4a- carbonized wood	1,314	0,965	1,024	0,494
4b- cellulignin de 0,5h	1,292	2,474	1,014	1,254
4c- cellulignin de 1,0h	1,327	1,452	1,002	0,727
4d- cellulignin de 2,0h	1,371	1,932	1,009	0,974
4e- double carbonization	1,421	2,497	1,000	1,248

(1) Picnometry of Helium; Equip. used: Ultrapicnometer - Model: 1000 from Quantachrome - Version: 1.62

(2) BET - Adsorption of N₂; Equip. used: Adsorptometer - Model: Nova from Quantachrome -Version 3.70

Samples	Porosimetry of Mercury D _p - Pore Diameter (nm)						Cylindrical Geometrl of the Pore (r = 2l) (SV)=(2πr ² + πrl)/(πrl) (SV) = (2l/r) S = 2V/r M ² /g	
	Average radius (nm)	D _p <10	10<D _p <100	100<D _p <1000	10 ³ <D _p <2x10 ³	2x10 ³ <D _p <5x10 ³		Total
3a- celluligin without grinding 0 > 2mm 0 > 354 μm	631,2 1026,2	0,016 0,004	0,078 0,022	0,233 0,084	0,038 0,039	0,056 0,048	0,421 0,197	2,968 0,758
3b- 297μm<0<384μm 210μm<0<250μm	893,0 987,2	0,008 0,009	0,033 0,027	0,095 0,084	0,052 0,048	0,046 0,051	0,232 0,219	2,080 1,755
3c- 177μm<0<210μm 149μm<0<177μm	845,8	0,003	0,018	0,094	0,062	0,035	0,212	2,004
3d- 125μm<0<149μm 105μm<0<125μm	1160,6	0,007	0,025	0,080	0,058	0,049	0,229	1,553
3e- 88μm<0<105μm 74μm<0<88μm	1003,2	0,009	0,025	0,091	0,051	0,042	0,218	1739
3e- 0<74μm	1716,4	0,008	0,023	0,108	0,163	0,530	0,830	3,876
								S = Surface of the pore V = Volume of the pore r = Radius of the pore l = Length of the pore

7 - The major application of the cellulignin of the present invention is as a fuel for boilers, gas turbine and for the generation of energy by magnet hydrodynamics (MHD). However, apart from the uses as a fuel, there are several other applications in the following areas: a volume component for animals food, pyrolysis for the production of oils and activated coal, production of carbon black (incomplete combustion), production of methanol, cellulignin resins (agglomerates, MDF - Medium Density Fiber), substrate for semisolid fermentation (fungi, bacteria and enzymes), etc.

Even though the precise chemical formula of the cellulignin according to the invention may vary, its empirical chemical formula is presented in Table 5, in comparison with the empirical formulas of wood, biomass components, mineral coal and fuel oils, these data providing a good reference for the understanding of the improved effects achieved by the fuel developed now.

Table 5: Chemical formulas of the several fuels

15	Fuel (moisture)	Material Volatile (%)	Carbon fixed (%)	Ashes (%)	Empirical formula approximate
	1. Soft wood (46%):				
	• Douglas fir	86,2	13,7	0,1	$C_{4,4}H_{6,3}O_{2,5}N_{0,1}$
	• Pitch pine	-	-	-	$C_{4,9}H_{7,2}O_{2,0}N_{0,1}$
20	• Hemlock	84,8	15,0	0,2	$C_{4,2}H_{6,4}O_{2,8}N_{0,1}$
	2. Hard wood (32%):				
	• Poplar	-	-	-	$C_{4,3}H_{6,3}O_{2,6}N_{0,1}$
	• White ash	-	-	-	$C_{4,1}H_{7,0}O_{2,7}N_{0,1}$
	3. Barks:				
25	• Oak	-	-	-	$C_{3,3}H_{5,4}O_{3,1}N_{0,1}$
	• Pine	-	-	-	$C_{4,5}H_{5,8}O_{2,4}N_{0,1}$
	4. Wood				
	• Dry (17%)	-	-	-	$C_{4,4}H_{6,0}$ $O_{2,4}N_{0,02}(H_2O)_{1,1}$
30	• Humid (50%)	-	-	-	$C_{4,4}H_{6,0}$ $O_{2,4}N_{0,022}(H_2O)_{5,6}$

Table 5 - continuation

fuel (moisture)	Material Volatile (%)	Carbon fixed (%)	Ashes (%)	Empirical formula approximate
5. Components of				
5 biomass:				
• Cellulose				$(C_6H_{10}O_5)_n$
• Hemicellulose				$(C_5H_{10}O_5)_n$
• Lignin				$(C_{10}H_7O_4)_n$
• Catalytic cellulignin				$C_{5.5}H_{4.2}O_{1.8}N_{0.7}$
10 • Cellulose coal				$C_{6.7}H_{3.3}O_{1.0}N_{0.7}$
6. Tar:				$C_{4.7}H_{5.8}O_{3.0}N_{0.7}$
7. Mineral coals:				
• Lignite (37%)	-	-	-	-
• Subbituminous				
15 A(14%)	-	-	-	-
B(25%)	40,7	54,4	4,9	$C_{6.0}H_{4.8}O_{1.0}N_{0.7}$
C(31%)	-	-	-	-
• Bituminous				
Low volatile	17,7	71,9	10,4	$C_{6.7}H_{4.3}O_{0.14}N_{0.11}$
20 Medium volatile	-	-	-	-
High volatile	6,4	81,4	12,2	$C_{6.8}H_{2.3}O_{0.12}N_{0.09}$
• Antracitic	6,4	81,4	12,2	$C_{6.8}H_{2.3}O_{0.12}N_{0.08}$
8. Oils (APF - A1)	-	-	-	$C_{7.3}H_{11.1}O_{0.09}N_{0.02}$

As can be seen, biomasses have low carbon contents (4.3 moles per formula-gram), middle hydrogen contents (6.5 moles per formula-gram), and high oxygen contents (6.5 moles per formula-gram). Mineral coals have high carbon contents (6.5 moles per formula-gram), low hydrogen contents (4.3 moles per formula-gram), and low oxygen contents (0.15 moles per formula-gram). The catalytic cellulignin according to the invention is in an intermediate position with carbon (5.5) and hydrogen (4.2) contents tending to mineral coal, but with intermediate oxygen contents (1.8 moles per formula-gram). In fact, the catalytic cellulignin comes close to lignite coal being obtained, however, in 20 minutes of pre-hydrolysis, while lignite coal took millions of years to be formed.

Another great advantage of the cellulignin fuel developed now is its very low ashes contents, thus meeting, for instance, the requirements of clean fuel for gas turbine ($\text{Na} + < 5 \text{ ppm}$) when processed in pre-hydrolysis with deionized water. This is due to the pre-hydrolysis process efficiency that solubilizes K in the form of water-soluble K_2SO_4 , which is later leached in the washing step. All impurities contained in the wood are reduced and even those of higher contents, such as Ca, Mg, Al, and Si present in eucalyptus wood, for example, do not cause hot corrosion on the superalloys of the gas turbines. The cycloning of the combustion gases from the fuel of the invention proved to be highly efficient in reducing the ashes contents at the level required for gas turbines (total particulate $< 200 \text{ ppm}$ and particulate with a diameter $> 5 \mu\text{m}$ being in a proportion lower than 8 ppm).

A few points should also be stressed with respect to the improved characteristics of the cellulignin fuel of the present invention, which bring expressive advantages for combustion processes, when compared to conventional fuels.

As already mentioned before, in the solid pyrolysis zone in a combustion process, high temperatures favor the production of volatile compounds, and low temperatures favor the production of coal. As already indicated by table 2 above, the products resulting from the cellulose and xylan pyrolysis result in high tar contents, which causes a secondary combustion close to the oils for wood. However, there is no xylan in the catalytic cellulignin according to the present invention, which leads to lower coal contents in this zone. It is further pointed out that the globulization of lignin in the production process of catalytic cellulignin fuel of the invention favors the formation of volatiles and decreases the coal contents. In addition, and considering the influence of moisture on the particle pyrolysis, it follows that the catalytic cellulignin fuel maximizes the combustion temperature, increases the volatile contents and decreases the formation of coal contents since provides the possibility of a burning without moisture and with low ashes contents.

Other technical advantages obtained according to the invention may be clearly observed during the pre-combustion reactions and in the primary combustion reactions, as well as in the post-combustion reactions of the cellulignin fuel.

In the pre-combustion step, it is observed that, in the case of the catalytic cellulignin, there is a decrease in the ash contents, the water contents and

xylans are non-existent, and these aspects favor CH_4 formation (a product from the decomposition of R⁺-cellulose) instead of C_2H_6 (product from the decomposition of hemicellulose, non-existent in cellulignin). During the primary combustion, the combustion of cellulignin takes place at higher temperatures, like the combustion of CH_4 resulting from the decarboxilation of the acetic acid and decarbonilation of the acetaldehyde resulting from the opening of the rings. This explains why, in practice, the catalytic cellulignin has a combustion similar to that of natural gas and of volatile liquid fuels. Finally, during the post-combustion step the ratio C:H is of 1:0.76 for the case of the catalytic cellulignin, that is to say, it is closer to the mineral coals than to wood. The average oxygen contents, however, favor the formation of CH_4 , CO_2 and CO , reinforcing the explanation for the high reactivity of the catalytic cellulignin.

In order to enable a better understanding of the similarity of the features of combustion of the catalytic cellulignin of the present invention as compared with those of the mineral coal, a modern theory of the combustion of porous particles (Essenhigh) is given below in view of its significance for the invention of the combustion of cellulignin.

The mass loss rate: $m = m(a, \sigma)$ wherein m = mass of the spherical particle, a = particle radius, $d = 2a$ = particle diameter, σ = particle density and $m = (4/3) \pi a^3 \sigma$.

$$\frac{dm}{dt} = \frac{\partial m}{\partial a} \frac{da}{dt} + \frac{\partial m}{\partial \sigma} \frac{d\sigma}{dt}$$

$$\frac{dm}{dt} = 4\pi a^2 \sigma \frac{da}{dt} + \frac{4}{3} \pi a^3 \frac{d\sigma}{dt}$$

$$R_s = \frac{dm/dt}{4\pi a^2} = \sigma \frac{da}{dt} + \frac{a}{3} \frac{d\sigma}{dt} = R_e + R_i = R_e \left[1 + \frac{R_i}{R_e} \right]$$

$$\frac{R_i}{R_e} = \frac{a}{3\sigma} \frac{d\sigma}{da} = \frac{1}{3} \frac{d(\ln \sigma)}{d(\ln a)}$$

20

R_e = mass loss rate by the external surface of the particle ($\text{g}/\text{cm}^2\text{s}$) e R_i is the mass loss rate by the internal surface. The above equation is an inexact differential equation impossible of being integrated due to the lack of a relationship between σ and the a (integration way).

Essenhig (1988) proposed the utilization of the equation of Thiele (1939) of catalysis as a way of integration of R_s

$$\frac{\sigma}{\sigma_0} = \left(\frac{d}{d_0} \right)^\alpha = \left(\frac{a}{a_0} \right)^\alpha \therefore \alpha = \frac{d(\ln \sigma)}{d(\ln a)}$$

- wherein $\alpha = 0$ stands for density, σ constant with combustion by the external surface and $\alpha \rightarrow \infty$ stands for constant diameter with combustion over the internal surface (This concept is similar to the catalysis over the external surface or over the internal surface).

Calculating the R_i/R_s relationship it follows that:

$$\frac{R_i}{R_s} = \frac{R_i}{R_m} \frac{R_m}{R_s} = \eta \frac{R_m}{R_s}$$

- wherein R_m is the maximum rate of internal loss and $\eta = R_i/R_m$ is the Thiele effectiveness factor ($0 < \eta < 1$) representing the relationship between the real internal loss and the maximum possible internal loss (For large particles or particles of low porosity, the internal mass loss is negligible and $\eta \rightarrow 0$ while for small particles and high density the internal loss of mass is maximum and $\eta = 1$).

- Defining S_v as the internal surface area per volume unit V_p ($(\text{cm}^2/\text{cm}^3) = 1/\text{cm}$) and S_p as the external surface area of the particle, it follows that the relationship R_m/R_s is proportional to the relation of the internal and external areas in:

$$\begin{aligned} \frac{R_m}{R_s} &= \frac{V_p S_v}{S_p} = \frac{\frac{4}{3} \pi r^3 S_v}{4 \pi r^2} = \frac{a S_v}{3} \\ \frac{R_i}{R_s} &= \frac{a}{3} S_v \eta = \frac{1}{3} \frac{d(\ln \sigma)}{d(\ln a)} = \frac{\alpha}{3} \\ \alpha &= a S_v \eta \end{aligned}$$

- For mineral coals, α ranges from zero to 3, exceptionally reaching the value of 6. For the catalytic cellulignin fuel, we have $S_v = \sigma S_p$, wherein \bar{S}_p is the in-

ternal surface per unit of mass, the following values resulting for a particle of 200 μm :

S_g	m^2/g	0,01	0,1	0,2	0,3	0,4	0,5	1,0	10,0
	m^2/kg	10	10^2	2×10^2	3×10^2	4×10^2	5×10^2	10^3	10^4
$\alpha = a\sigma S_g \eta$		1	10	20	30	40	50	100	1000
$(\sigma/\sigma_0) = (d/d_0)\alpha$ $p/(d/d_0) = 0,9$		0,9	0,349	0,122	0,042	0,015	0,005	$2,7 \times 10^{-5}$	$1,7 \times 10^{-6}$

- This means that for a specific surface larger than $0,4 \text{ m}^2/\text{g}$ ($\alpha = 40$),
- 5 the catalytic cellulignin fuel burns mainly from the internal surface, maintaining the particle diameter approximately constant and varying its density (burning of a fractal - 1st zone), characterizing the new invention as a large-scale, completely catalytic, fuel obtained from the pre-hydrolysis of biomass available in nature. Tests of specific surface (BET, porosimetry of mercury and MEV) indicate an average value of
- 10 $2,0 \text{ m}^2/\text{g}$, resulting in $\alpha = 200$. The particles of liquid fuel burn from the external surface ($\alpha = 0 - 3^{\text{rd}}$ zone), and the particles of mineral coal have partial internal combustion ($0 = \text{or } < \alpha = \text{or } < 3 - 2^{\text{nd}}$ zone).

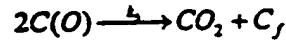
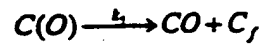
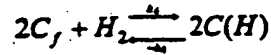
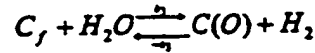
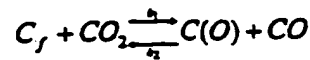
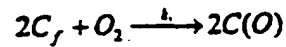
- For the case of mineral coal, $\alpha = S_v/\gamma$, wherein γ is the Thiele parameter given by:

15
$$\lambda = (S_v \bar{\kappa} / \rho D_e)^{1/2}; \alpha = (\rho D_e S_v / \bar{\kappa})^{1/2}$$

wherein k = constant of the reaction rate, ρ = reactive gas density and D_e = coefficient of internal diffusion. For the catalytic cellulignin there is no need for independent determination of these parameters, because they combine, resulting in a relatively high value of α ($\alpha = \text{or } > 100$).

- 20 - In the catalytic combustion, the oxygen does the direct attack on the carbon atom as a two-stage reaction (adsorption-desorption), illustrated in figure 5. Oxygen is adsorbed and desorbed, forming CO_2 or CO , which is then desorbed.

The components and products of the reaction are C, O₂, CO₂, H₂O, H₂, and CO, ac-



according to the following reactions:

wherein C_f indicates a free site, C(O) stands for a chemically adsorbed oxygen atom and k_i are reaction constants. The volatiles (CO, H₂) produced by the catalytic combustion complete their combustion outside the particle with a very short combustion time (3 ms). The determined combustion time is that of the adsorption-deadsorption process, being equal to or shorter than 20 ms (0.02s) for the catalytic cellulignin.

The burning time for mineral coal, liquids (oils) and for catalytic cellulignin fuel measured in the form of isolated particle and in the form of powder cloud is illustrated in figure 6 and the formulas utilized in the corresponding calculations are presented below.

Attachment I: Combustion Times

1a - Coal Combustion

15

Burning time

i) at constant density:

$$t_b = \frac{\rho_0 RT_m}{96\phi Dp_s} d_0^2$$

ii) at constant diameter

$$t_b = \frac{\rho_0 RT_m}{144\phi Dp_s} d_0^2$$

wherein:

ρ_0 = initial density of the particle $\cong 1000 \text{ kg/m}^3$

R = universal constant of the gases = $0,8106 \text{ m}^3 \text{ atm}/(\text{kmolK})$

T_m = average temperature = 1600 K

5 D = diffusion coefficient = $3,49 \times 10^{-4} \text{ m}^2/\text{s}$

P_o = partial oxygen pressure = $0,2 \text{ atm}$

ϕ = order of reaction = 2

d_0 = initial particle diameter (m)

1b - Combustion of Liquids

10 Burning time

$$t_b = \frac{d_0^2}{\lambda}$$

wherein:

d_0 = initial diameter

λ = evaporation rate = $10 \pm 2 \times 10^{-3} \text{ cm}^2/\text{s}$ for hydrocarbons burning in air.

15 In the first form, the burning time is shorter than that of mineral coal because it is a much more reactive fuel. In the form of a powder "cloud", there is a decrease in the thermal losses due to the energy transmission by radiation among the particles, decreasing the burning time for values similar to those of the volatile liquids. One way of analyzing this question is by means of the Krishna and Bertad's

20 energy balance for ignition of powder cloud of mineral coal.

$$(\text{const}) T_i^{p-1} = \frac{\lambda_0 / a}{1 + R^2 D / a^2 \sigma}$$

wherein the first term is the energy generation rate, a is the radius of the particle, R is the radius of the cloud, ρ is the particle density, D is the density of the cloud, λ_0 is the air thermal conductivity and β is an empirical coefficient. If $R^2D/a^2\sigma \ll 1$ it follows that $aT_{\beta}^{-1} = (\text{const.})$ and if $R^2D/a^2\sigma \gg 1$, then $T_{\beta}^{-1} = (\text{const.})a$. The latter is in accordance with the world experience that recommends grinding the mineral coal at temperatures not higher than 70°C to avoid incineration of the powder cloud in the mills. For catalytic cellulignin fuel injection, we have $R = 0.1\text{m}$, $a = 100 \times 10^{-6}\text{m}$, $\sigma = 500\text{ kg/m}^3$, $D = 0.4\text{ kg/m}^3$ resulting in $R^2D/a^2\sigma = 800 \gg 1$. The smaller the particle size, the lower the ignition temperature of the powder cloud. For mineral coal, the theoretical ignition temperature of the cloud is 300 at 500°C and for catalytic cellulignin, the ignition temperature is on the order of 350°C (pyrolysis temperature). The presence of oxygen in the molecule of the catalytic cellulignin fuel favors the similarity of its combustion process to that of mineral coal (however, with higher reactivity and higher ignition temperature) with respect to the combustion of wood, which is of five steps and seriously limited by the presence of water.

In order to establish the combustion characteristics, catalytic cellulignin particles of different diameters were burned by means of LASER ray ignition and determination of irradiation intensity with photodiodes. The results are shown in figures 7a and 7b, where one can see two regimes, namely: 1) above $250\mu\text{m}$ the combustion is of the conventional type (limited by the transport of mass inwards and outside the particle) and 2) below $25\mu\text{m}$ the combustion is not limited by mass flow (process of adsorption of O_2 - desorption of CO). The two regimes adjust to Thiele's catalytic combustion. Attention is drawn to the importance of maintaining the crystalline characteristic of the cellulose in the pre-hydrolysis process to render the grinding of cellulignin particles smaller than $250\mu\text{m}$ inexpensive.

a) Conventional combustion ($\phi > 250\mu\text{m}$): the catalytic cellulignin is dried outside the combustion equipment and the drying zone is non-existent. The heating is rapid, the generation of volatiles is maximized while coal generation is minimized. The catalytic cellulignin does not contain xylan, its solid pyrolysis predominating, that is to say, opening of the ring with production of acetic acid, acetaldehyde and coal by decarbonilation of the acetic acid and decarboxylation of the acetaldehyde in the formation of CH_4 , CO_2 and CO . The zones of volatiles primary and secondary combustion are the same as described before.

b) Catalytic combustion ($\phi < 250\mu\text{m}$): The pre-hydrolysis displaces the biomass in the direction of the combustion of mineral coal. The main characteristic is that combustion is more limited by the mechanism of the oxygen transport into the catalytic cellulignin and of CO therefrom due to the particle microstructure. In this way, there physical (O_2) and chemical (O) adsorption in active sites and Boudouard's reaction is favored. Reactions of hydroxylic groups cause rapid reactions in the heating and solid pyrolysis zones. The catalytic combustion occurs in the average internal surface ($2.0\text{m}^2/\text{g}$), the contribution of the external surface ($0.1\text{m}^2/\text{g}$) of the particle being secondary. The framework of the catalytic cellulignin is that of a fractal that burns while maintaining the diameter of the particle approximately constant and decreasing the particle density. When the wall of the fractal thickness reaches a critical size, a collapse of the particle (sublimation) takes place. Therefore, the process eliminates the formation of residual coal, resulting in complete combustion.

15 The combustion equipment usable for the catalytic cellulignin of the present invention will depend upon the type of specific combustion to be employed. In this regard, the main methods of biomass combustion are: combustion in pile, thrower-spreader, suspension, and fluidized bed, the thrower-spreader combustor is the most prominent from the industrial point of view. The characteristic of the first two is the complete physical separation of the five combustion zones. In the combustion by suspension of dry biomass particle ($\phi < 2\text{mm}$, $\text{TU} < 15\%$), all "zones" take place in the middle of the air, in a sequential way. The suspension burning is the closest to the burning of liquid fuels. This is the case of the cellulignin proposed now, which comes close to the combustion of gases and liquids due to its catalytic combustion.

25 The combustion in fluidized bed maintains the fuel in a bed with sand or lime suspended by air. All the reaction zones take place in the same place (not separable physically). The combustion efficiency is low due to the excess air (100 - 140%) necessary to maintain the fluidized bed, and the temperature is kept below the ashes melting point in order not to cause the bed to collapse. In the case of the catalytic cellulignin of the invention, the suspension combustion may be carried out with stoichiometric air and without limitation of temperature, since it has a very low

ash content. The three main parameters in the combustion are useful heat, thermal efficiency and combustion temperature.

$$H_v = CCS - PT; \eta = [1 - (PT/CCS)] \times 100$$

wherein CCS is the upper calorific capacity and PT are the thermal chimney losses, ashes (including not-burnt carbon), radiation and others. The chimney losses are given by:

$$PT = \sum_{i=1}^n m_i (C_{p,i} \Delta T) + m_{H_2O} \lambda_{H_2O}$$

wherein m_i is the moles of the chimney gases (CO_2 , O_2 , N_2 , H_2O), $C_{p,i}$ is the calorific capacity of each species, ΔT is the difference in temperature between the chimney and the environment, m_{H_2O} is the number of moles of water and λ_{H_2O} is the molar water vaporization value.

The losses by radiation are of about 4% and other losses (ash, not-burnt carbon) are about 2%. The combustion efficiency of a wood with 50% moisture is 68%; with 17% moisture, it is 79%, and that of the catalytic cellulignin is 85% (close to the values of the mineral coal) due to the absence of moisture, ash and excess air. The catalytic cellulignin fuel of the invention permits the achievement of temperatures close to the adiabatic one (1920 K), although the temperatures of the vapor-generating tubes of the boilers are limited to 840K.

The heat release rates for the different combustion methods are given by $I = h \, dW/dt$, wherein I is the flame intensity, dW/dt is the change in weight in function of the time, and h is the combustion heat. Table 6 shows several rates for the different combustion methods:

Table 6: Heat release rates for different combustion methods.

Combustion method	Wood	Mineral coal
Combustion in pile	8,5GJ/m ² h	
Inclined grid	3,5GJ/m ² h	
Thrower-spreader	10,4GJ/m ² h	8,8GJ/m ² h

Suspension	550GJ/m ³ h	
Fluid bed	470GJ/m ³ h	

The reactivity of the catalytic cellulignin is slightly higher than that of biomass (absence of water, larger specific surface) and the combustion heat is the double, leading to a heat release rate twice as high as that of wood. For example,
 5 9kg/h of catalytic cellulignin with combustion heat of 20MJ/jg burn in suspension in a volume of $\phi = 2\text{cm}$ and $L = 50\text{cm}$, that is, $(9 \times 20) / (\pi \times (0,01)^2 \times 0,5) = 1.146\text{GJ/m}^3\text{h}$.

The examples of equipment given below will better illustrate the present invention in a better way. However, the data and procedures illustrated merely refer to a few embodiments of the present invention and should not be taken as being
 10 limiting of the scope of the invention.

The complete characterization of the catalytic cellulignin fuel involves elements of the cellulignin as starting material, of the combustion specific characteristics and of the fuel handling and controlling equipments.

Figure 8 illustrates a feeding system composed of a cellulignin tank
 15 (8.1), a rotary valve or helical feeder for dosing the cellulignin feed (8.5 and figures 9 and 10), feeding line of the air/cellulignin two-phase fluid (rate 3.28:1 by weight) (8.6) and applications in boilers and ovens (pressure close to the atmospheric one, $T = 1900^\circ\text{C}$), in gas turbines (pressure of 7 - 14 atm, $T = 600 - 1100^\circ\text{C}$). The cellulignin tank may be either stationary (preferably in vertical cylindrical form), or move-
 20 able (installed in carriage similar to the tanks for carrying animal food or cement). Due to the tendency of cellulignin to settle, the tanks are preferably provided with a conic or plane bottom and with powder handlers of the rotary-shovel type (8.2, 8.3, 8.4), helical feeders or a bottom with moveable compressed-air lining. At the exit of the rotary valve or helical feeder for dosing the cellulignin, drag air is injected for
 25 two-phase flow at the ratio of 3.28:1. The two-phase flow may be made of metallic, plastic pipes or hoses, the air/cellulignin mixture behaving as if it were a gas or a liquid. Under low pressure, the energetic density of the air/cellulignin mixture is of 7.14MJ/m³, while that of natural gas is 32.9MJ/m³ and that of the fuel oils is 28.0MJ/m³, permitting still compact, simple installations and significant lengths of

the piping, in order to meet the layouts of the factories, thermoelectric power stations, etc.

The helical feeder shown in figure 9 is composed of a body (9.1), bushing (9.2), helical feeder (9.3), powder retainer (9.4), bearings (9.5), flanges (9.6), driving pulley (9.7) and air injection for two-phase flow (9.8). The dosage of cellulignin is carried out by turning the helical feeder and varying its diameter and, in general, it is utilized for low capacities (<150 kg/h). The elimination of the influence of pressure difference between the cellulignin tank and the drag gas in dosing the powder carried by the helical feeder is carried out by means of the impedance of the length of the helical feeder between the tank body and the drag air of the two-phase flow. The rotary valves illustrated in figure 10 are available on the market for capacities higher than 150 kg/h and comprise a body (10.1), shovels (10.2), driving shaft (10.3), inspection window (10.4) and possibly cooling (10.5). The dosage is made by means of rotation, the diameter and the length of the valves.

15 Combustors

The direct use of combustors in boilers and ovens is possible because of the low content of the cellulignin ashes ($<0.2\%$) and the resources already existing in this equipment for removing residual ashes. For applications in gas turbines, the following measures are necessary: a) combustion chamber with injection of primary air (stoichiometric combustion) and secondary air (drag of the ashes from the combustion chamber to the cyclone and cooling of the combustion gases down to the working temperature of the turbine); b) gas-cleaning cyclone (removal of the particulate); and c) possible ceramic filter for high temperature turbines (1100°C - monocrystalline superalloys), and these filters are indispensable to polycrystalline superalloys or with directional solidification. The specifications of $\text{Na} + \text{K} < 5\text{ppm}$, in the catalytic cellulignin fuel with total particulate contents of 200ppm , with diameter $> 5\mu\text{m}$ lesser than 8ppm in the combustion gases, have been achieved without the need for ceramic filters.

Axial Combustor

30 Figure 11 shows an example of an axial combustor to characterize the combustion of the catalytic cellulignin. The ignition may be carried out in several

ways, such as by microblowtorches of GLP, natural gas, etc., electric arc, electric resistance or hot gas tube. The fact that it is easy, automation and low cost favor the ignition with blowtorches of GLP, natural gas (consumption of 0.022 kg of GLP/kg of cellulignin, representing 5% of the calorific capacity of the combustor). Two factors
5 related to catalytic cellulignin ignition are pointed out: first, the need for it to be heated up to the pyrolysis temperature (350° C); second, the operational security of the catalytic cellulignin with respect to the combustible gases and liquids that ignites at room temperature. The practical applications may be made with any type of combustor (axial, swirler, cyclonic, etc.)

10 The axial combustor is composed of a mounting plate (11.1) with or without cooling, cellulignin injector (11.2), stoichiometric-combustion-air injector (11.3), fixture of the ignition blowtorches (11.4) with or without cooling, ignition blowtorch of GLP, natural gas, etc. (11.5), window with view-finder (11.6). Ignition
15 blowtorches are as small as available on the market, because the catalytic characteristics of cellulignin enable their instantaneous ignition and propagation for the two-phase air/cellulignin flow. The power of the ignition blowtorch is on the order of 5% of the power for low capacity (50kW) combustors and tends to negligible percentages for high capacity combustors. For the two-phase flow with velocity of 8.5m/s and a diameter $\phi = 16.5$ mm, the ignition spreads at a length of 100 mm,
20 giving an ignition time of $0.012s = 12ms$. The combustion is complete at a length of 0.7m, giving a residence time of $1/(8.5/2) = 0.16s = 160ms$ (one has utilized the average velocity of $8.5/2 = 4.25m/s$, since the injection velocity in the beginning of the flame is of 8.5m/s and the velocity at the end of the flame is virtually nil). The resistance-time/ignition-time relationship is on the order of ten times. The ignition times of
25 the catalytic cellulignin tend to the ignition times of gases, which are on the order of 3ms.

In general, mineral coal and liquid fuels generate a very long flame length, due to the longer burning times (see figure 6), thus requiring combustors of the axial-swirler type for reducing the flame length. The catalytic characteristic of
30 cellulignin allows one to use axial combustors with relatively short flame lengths. The extinguishing of the ignition blowtorch results in extinguishing the flame of the catalytic cellulignin, due to the need for it to be pyrolyzed at 35° C, imparting to the catalytic cellulignin complete security in its handling (non-incendiary and non-

explosive fuel). The catalytic cellulignin does not contain hemicellulose, which is responsible for the incendiary characteristic of biomasses in the form of straws (pyrolysis temperature = 200° C), as well as it does not pyrolyze at low temperature, and so does not have the incendiary characteristics of the gases and liquid fuels (low flash point). On the other hand, above 350° C, its combustion is catalytic with ignition times close to that of gases.

Gas Turbines

For applications of cellulignin combustors in gas turbines, two additional steps are required, namely: cooling of the gases and a cyclone for reducing particulates. Figures 12a and 12b show the cellulignin combustor, cycloning and particulate collector with horizontal or vertical assembly. It is composed of combustor (12.1), combustion chamber (12.2), inlet of cooling air (12.3), chamber of cooling air (12.4), homogenization sector (12.5), cyclone (12.6), particulate collector (12.7), and duct of connection with the turbine (12.8). In the vertical position, an ash collector (12.9) is added before the combustion gases are directed to the cyclone for collection of the molten ashes during the stoichiometric combustion.

The combustor illustrated is manufactured from stainless steel, except for the combustion chamber, which is made from superalloys due to the high temperatures (1920°K), being cooled by the cooling air. A portion of the cooling air penetrates the bores in the wall of the combustion chamber, creating a peripheral layer of drag air for dragging the molten ashes and particulates.

One of the main characteristics of the gas turbines is their versatility with regard to fuels, operating with gases such as natural gas, evaporated oils and process gases (refineries, blast-furnaces and gasifiers); liquids such as clean liquids that are volatile Naphthas, light distillates (Diesel, kerosene) and viscous and heavy residual oils; and solids. Liquid fuels with high ash contents (crude and residual oils) require cleaning equipment prior to their utilization.

Table 7 illustrates the properties of the three types of conventional fuels and of the catalytic cellulignin. The latter is placed between the natural gas and light distillates (clean fuels) and the mixtures of heavy distillates and low-ash crude oil. It does not contain V_2O_5 , WO_3 , MO_3 , or Pb, and the S content is very low. The Na

+ K for the clean catalytic cellulignin concentration is close to that of the clean fuels while for normal catalytic cellulignin it is close to that of heavy residual high-ash crude oils (table 8). The pre-hydrolysis carried out with deionized water is an effective technology of producing the clean catalytic cellulignin as a fuel for gas turbines.

- 5 The only parameter out the conditions of clean fuel is the total ash contents (< 0.1%). These are, however, significantly reduced in the cyclone, reaching total particulate contents < 200ppm, and contents lower than 8ppm for particles with size bigger than 5 μ m.

- Natural gas distillates do not need a fuel treatment. Mixtures of heavy
10 distillates, low-ash crude oils and especially heavy residual high-ash crudes need washing of the fuel that is based on the water-solubility of sodium, potassium, and calcium. There are four conventional washing processes, namely: centrifuge, D.C. electric, A.C. electric, and hybrid. The catalytic cellulignin dispenses with any wash-
15 ing process that has been used for reducing the Na + K contents from 100ppm down to levels of from 5 to 0.5ppm in crude and residual oils.

Table 7: Properties of the Fuels

Table 7: Properties of the Fuels												
Properties	Distillates and Naphtha				Catalytic lignin		Cellu-		Mixtures of Distillates a Low Ash			High Ash Crude and Heavy Residues
	Kero-sene	#2	Oil #2	JP-4	Clean	Normal	Low Ash crude	Typical Crude from Libia	Heavy Distillates			
Flash Point (° C)	54/71	48/104	66/93	<T.A. (1)	350 (2)	350 (2)	10/93	-	92		79/129	
Flow Point (° C)	- 45	-48/-12	-23/-1	-	Any (3)	Any (3)	-9/43	20	-		-9/35	
Visc. CS to 38 ° C	1.4/2.2	2.48	2,0/4,0	0,79	(4)	(4)	2/100	7,3	6,20		100/1800	
SSU	-	2,67	-	-	-	-	-	-	-		-	
Grau API	-	34,4	-	53,2	-	-	-	-	-		-	
Sécol Desn. at 38°C	0,78/0,83	38,1	35,0	0,7545 (5)	0,50	0,50	0,80/0,92	0,84	0,8786		0,92/1,05	
Calorific Power MJ/kg	44,6/45,5	42,3	43,9/45,3	20,0		20,0	43,9/44,8	42,2	42,1		42,3/43,7	
Ashes	1 a 5	0,001	0 a 20	-	1000	2000	20 a 200	36	-		100/1000	
Coal Residues	0,01/01	0,104	0,03/0,3	-			0,3/3	2/10	-		-	
Sulfure (%)	0,01/0,1	0,164 a	0,1/0,8	0,047	<80 ppm	280 ppm	0,1/2,7	0,15	1,075		0,5/0,4	
Hydrogen	12,8 / 14,5	12,83	12,0/13,2	14,75	4,3	4,3	12,0/13,2	-	12,40		10,0/12,5	
Na + K (ppm)	0/1,5	-	0/1,0	-	5	<60	0/50	2,2/4,5	-		1/350	
Vanadium	0/0,1	-	0/0,1	-	Zero	Zero	0/15	0/1,0	-		5/400	
Lead	0/0,5	-	0/1,0	-	Zero	Zero	-	-	-		0/25,0	
Calcium	0/1,0	0/2,0	0/2,0	-	<500	500	-	-	-		0/50	

Properties	Distillates and Naphtha	Catalytic Cellulignin	Mixtures of Distillates and Low Pressure Crude	High Ash Crude and Heavy Residues
Preheating of the fuel	No	No	Yes	Yes
Atomization	Mechanics/ Low Pressure Air	No	Low Pressure/ High Pressure Air	High Pressure Air
Disalination	No	No	Some	Yes
Inhibitor	No	No (Limited)	Limited	Always
Washing of the Turbine	No	No	Yes (except for distillate)	Yes
Initial Fuel	With Naphtha	Ignition (GLP, natural gas, heated tubes, electric resistance)	Some Fuels	Always
Cost	Higher	Intermediate	Intermediate	Lower
Description	Low-quality Distillate free of ashes	Porous powder with limited ash contents, that can be reduced by cyclones	Low Ash, Limited Level of Contaminants	High Ash Low Volatility
Designation ASTM	1GT, 2GT, 3GT	(3-GT)	3GT	4GT
Turbine Inlet Temperature	Higher	Intermediate	Intermediate	Low

Table 8 – Inorganic impurities (mg/g) of Eucalyptus, Catalytic Cellulignin and Pre-hydrolysate

	Ca	K	Na	Mg	P	Al	Si	Mn	Fe	Zn	S
Eucalipto	560	400	<140	160	170	50	<120	20	10	ND	140
Celulignina normal (1)	500	<60	<140	<40	10	<40	<120	<4	<10	<6	<80
Celulignina limpa (2)	<53	<5	<1	<60	<2	<40	<120	<2	<7	<4	<80
Pré-hidroli-sado (3)	260	370	80	140	65	10	25	20	8	5	1950

(1) cellulignin processed with filtered tap water, with X-rays semi-qualitative analysis

5 (2) cellulignin processed with deionized, with X-rays semi-qualitative analysis except for K (by ICP/AES) and Na (AAS-flame)

(3) mass balance not carried out due to the absence of initial water and washing water analysis.

10 For gas turbines, specifications of the fuel level are usually made. In the case of catalytic cellulignin, due to the purification of the cyclones coupled to the combustor outside the turbine, the specifications should be made at the level of the combustion gases or in terms of an "equivalent fuel".

The influence of the (Na + K) contents (ppm) on the working temperature of the Inconel superalloy 718 is given by:

(Na + K) ppm	0,33	2,28	3,70	4,89	5,65
Temperature (°C)	927	871	815	760	704

15

20 The catalytic cellulignin fuel allows operation in the range of 800 to 830°C. Coatings are utilized in order to increase the resistance of the superalloys to hot corrosion. Table 8 shows the main types of coating obtained by diffusion (Al, Pt, Rh, NiCrSi) and by overlayers (Co, Cr, Al, Y). Various techniques of depositing the overlayers are utilized, namely: plasma spray, sputtering, deposition of vapor by electronic beam (PVD) and cladding. At present, the hot-corrosion resistances are limited by the coatings and not by the base-metals of the rotors and stators of the turbines.

The protection with plasma or EB/PVD, however, enables one to achieve 16000h of operation, even under aggressive conditions.

The main requirements for a gas turbine fuel are: calorific power, cleanliness, corrosivity, deposition/obstruction and availability. The fuel from clean catalytic cellulignin obtained by pre-hydrolysis from biomass with deionized water meets all the above requirements.

Table 9: Protecting Layers (coatings) of the Turbines

Specification of the Protection	Element in the Layer	Deposit technique	Typical applications	Capacity in hours: Combustion chamber (870°C)
UC	Al	PC	Co Base stators of	
870	Al,Si	PC	Base parts Ni	
RT-5	Al,Cr	DPC	Ni Base stators	
RT-17	Al,Ni	DPC	Nickel doped with Thorium	
RT-19	Al	DPC	Co Base stators (High temperature service)	
RT-21	Pt,Al	PC	Ni stators and rotors	800
RT-22	Rh,Al	EP/PC	Ni base rotors	5000
BB	Pt,Rh,Al	EP/PC	Ni and Co Base stators and rotors	
RT-44	Co,Cr,Al, Y	EB/PVD	Co Base stators	
Overlayers	Ni,Co,Cr, Al	EB/PVD	Overlayers for various services	7000 (plasma) 14000 (composed plasma) 18000 (clad)

PC – Pack Cementation; DPC – Double Pack Cementation; EP – Eletroplating; EB – Electron Beam; PVD – Physical Vapor Deposition

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CLAIMS

1. A catalytic cellulignin fuel, characterized in that it is composed of cellulose and globulized lignin with specific surface of about 1.5 - 2.5 m²/g.

2. A catalytic cellulignin fuel according to claim 1, characterized in that it is composed of cellulose and globulized lignin with an average specific surface of about 2 m²/g.

3. A cellulignin fuel according to claim 1 or 2, characterized in that it has a heat combustion value of about 18 to 20 MJ/kg.

4. A cellulignin fuel according to any one of claims 1 to 3, characterized in that it is ground into particles having size lower than 250 nm.

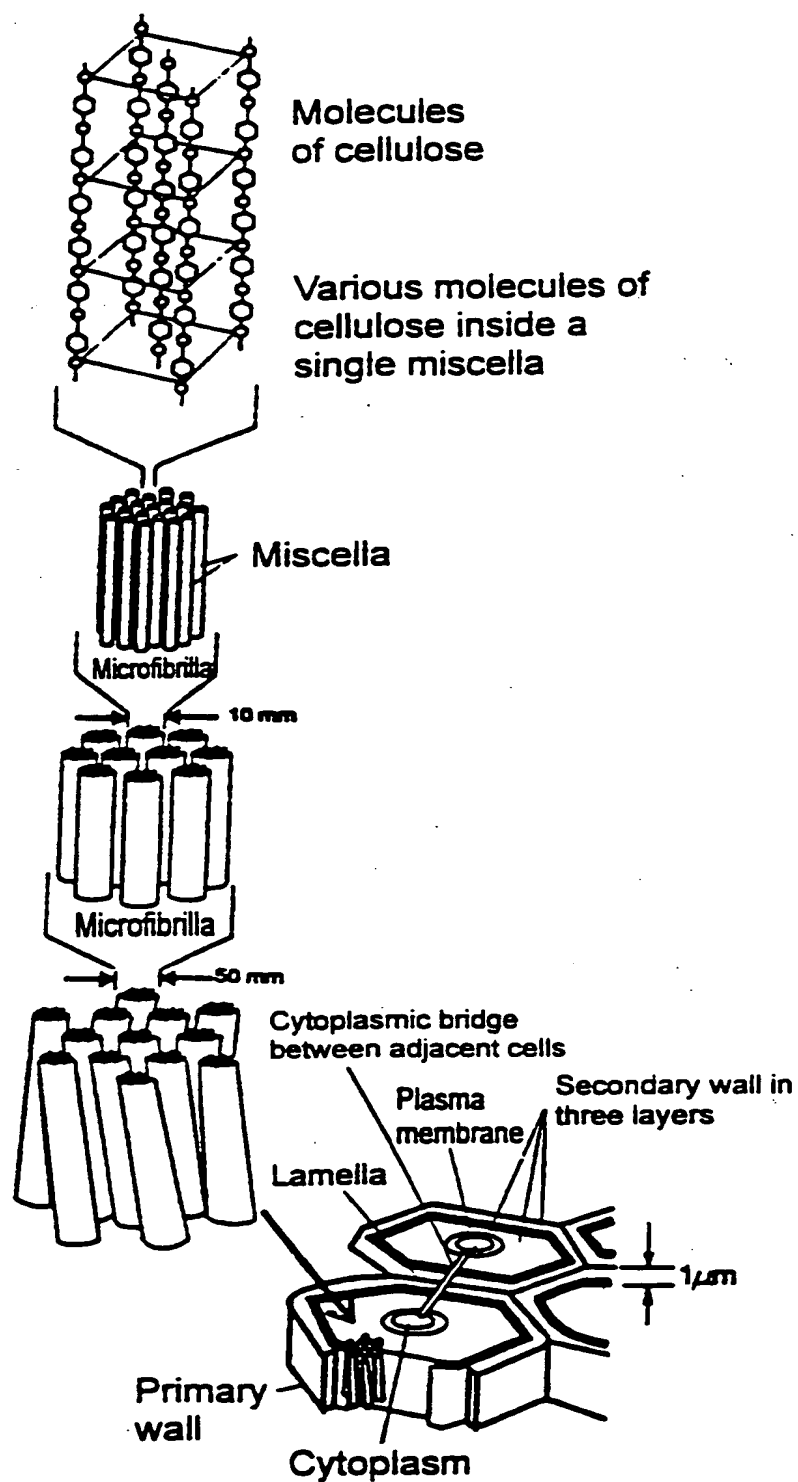
5. A cellulignin fuel according to any of the preceding claims, characterized in that it presents an ignition time equal to or shorter than 20 ms (0.02s).

6. A cellulignin fuel according to any one of the preceding claims, characterized in that it has a volatilization temperature of about 350° C.

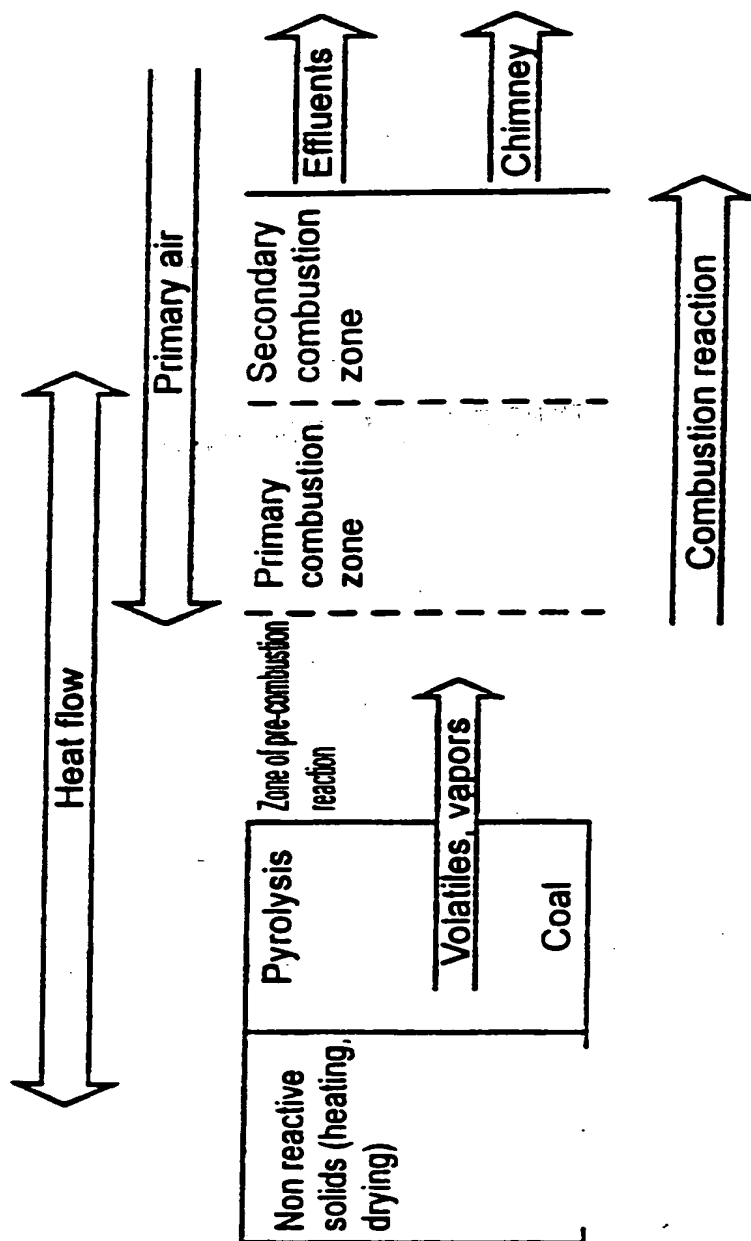
7. A cellulignin fuel according to any one of the preceding claims, characterized by a Na + K content lower than or equal to 5 ppm.

8. A cellulignin fuel according to any one of the preceding claims, characterized in that it generates combustion gases with total particulates lower than 200 ppm, the particles having diameter lower than 5 nm at concentrations lower than 8 ppm.

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**FIG 1** Cellular structure of biomass

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Conceptual model of the combustion of solid fuels.
Complexity of the combustion of wood

FIG 2

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Fig 3a

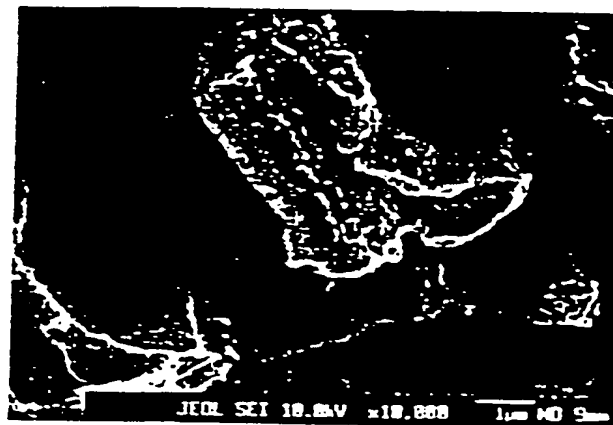


Fig 3b

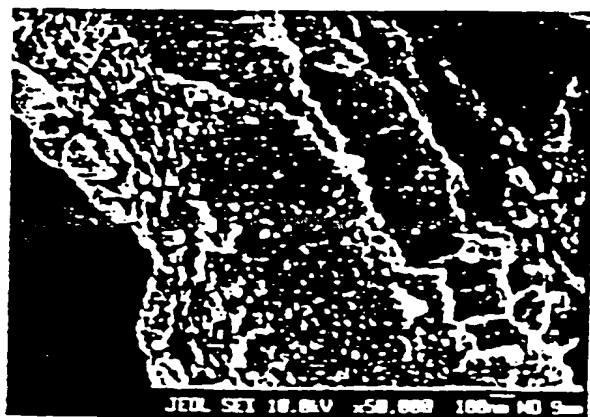


Fig 3c

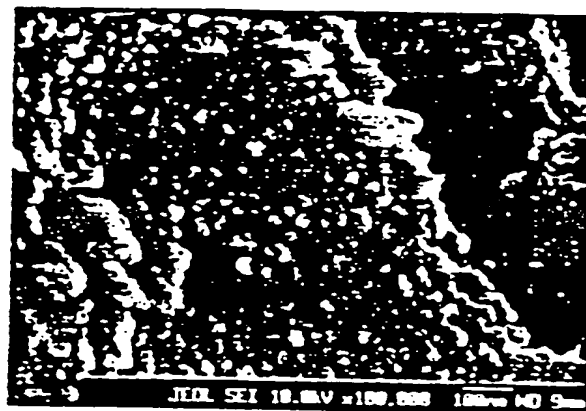


Fig 3d

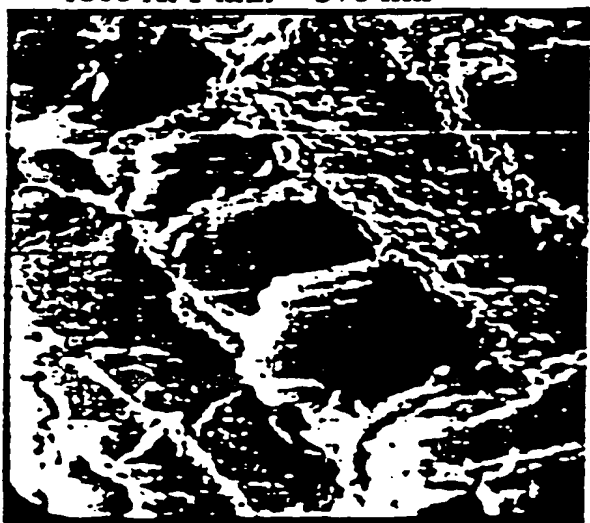
4/11



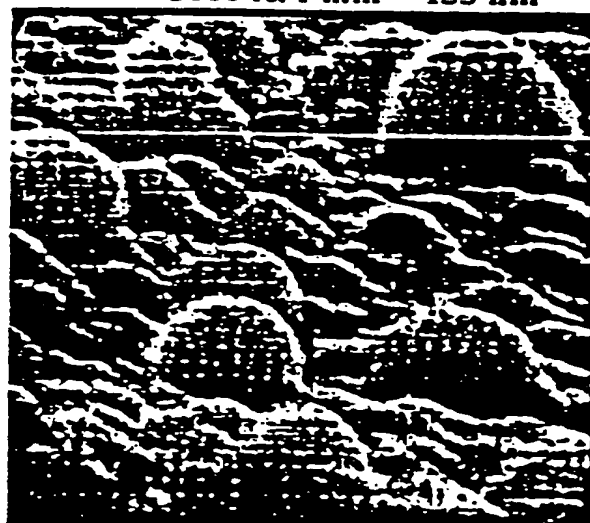
1800 X. 1 mm = 370 nm



5000 X. 1 mm = 133 nm



2000 X. 1 mm = 333 nm



20.000 X. 1 mm = 33 nm

Fig 3e: Microstructure of the cellulignin with globalized lignin

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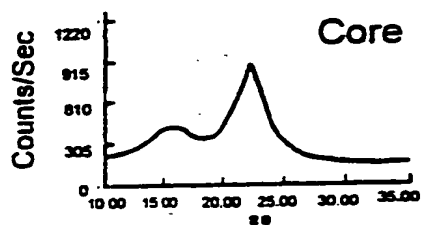
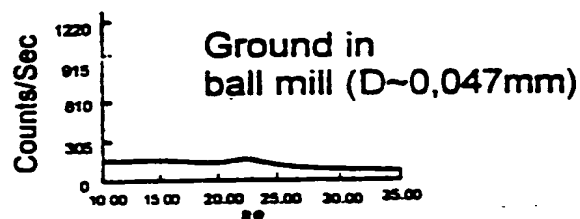
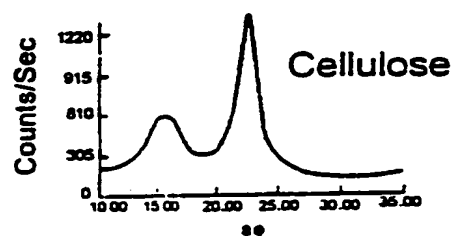
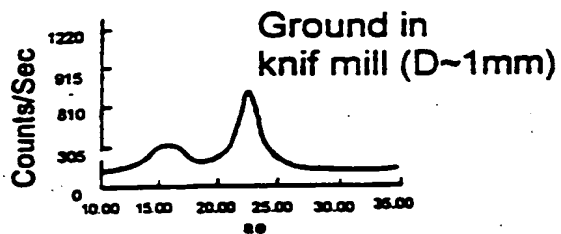
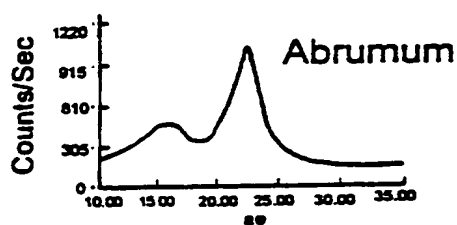
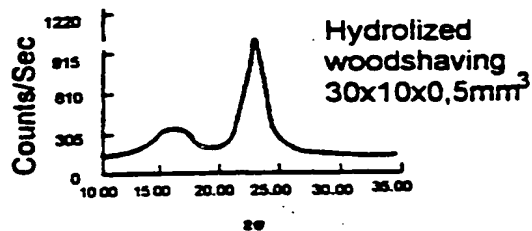
Diffraction of X-ray of wood
and eucalyptus celluloseDiffraction of X-ray
for cellulignin

FIG 4 X-Ray diffratogram for wood, cellulose and cellulignin

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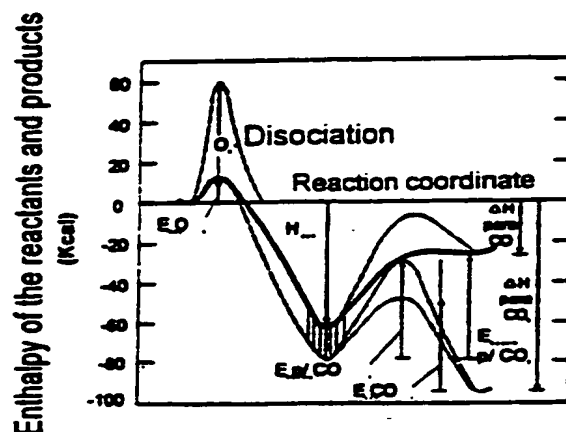


FIG 5 Variation of the Enthalpy of the Reactants and products the coordinate of the Carbon-Oxygen reaction.

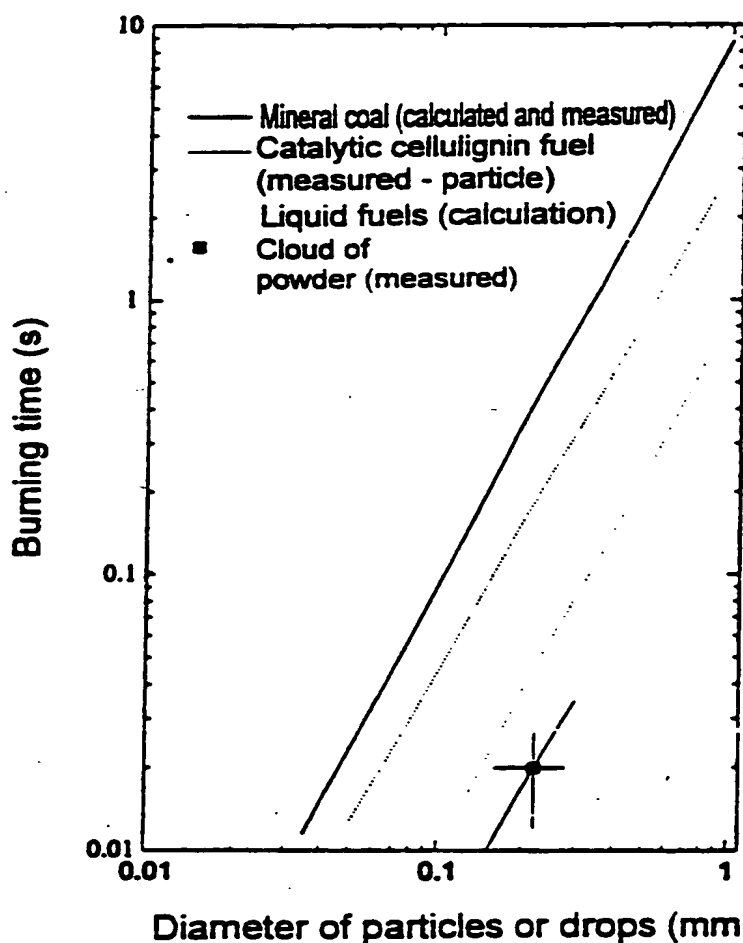


FIG 6 Burning time versus Diameter of particle for mineral coal, catalytic cellulignin fuel, particle and in powder cloud and liquid fuels

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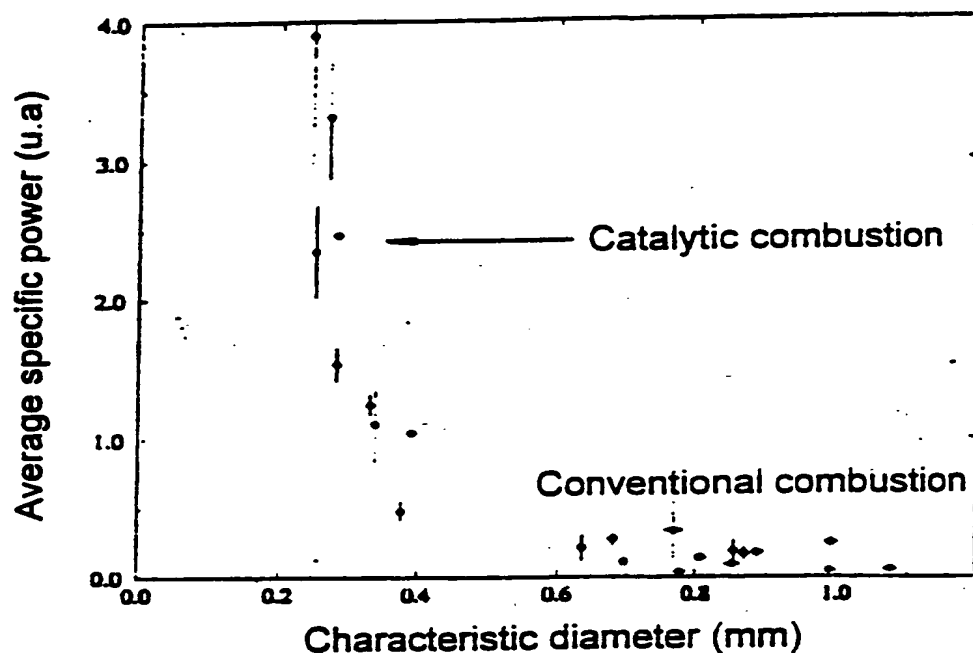


FIG 7a Average specific power irradiated in the combustion
a Catalytic Cellulignin particle (linear scale)

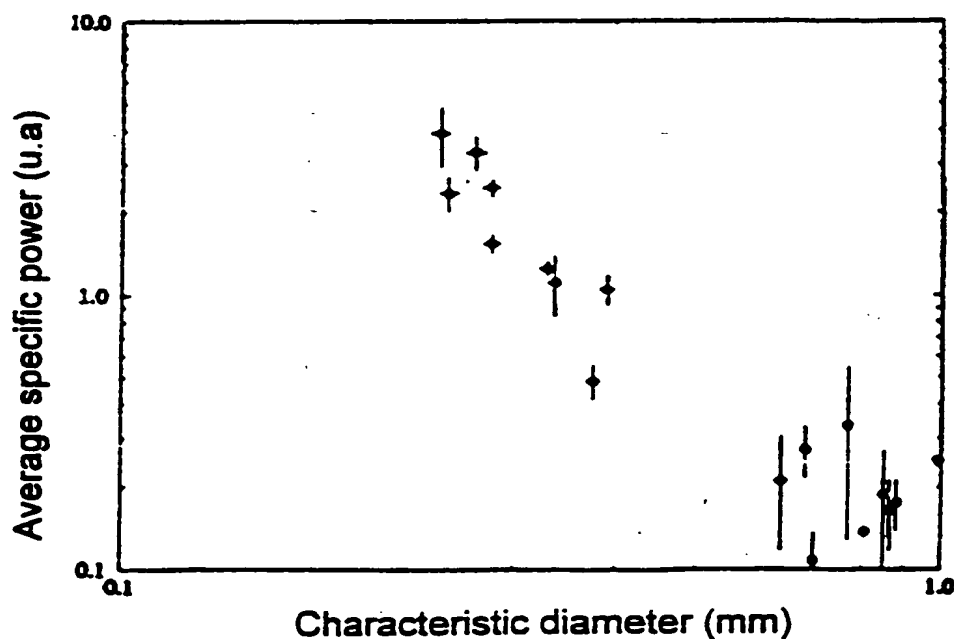
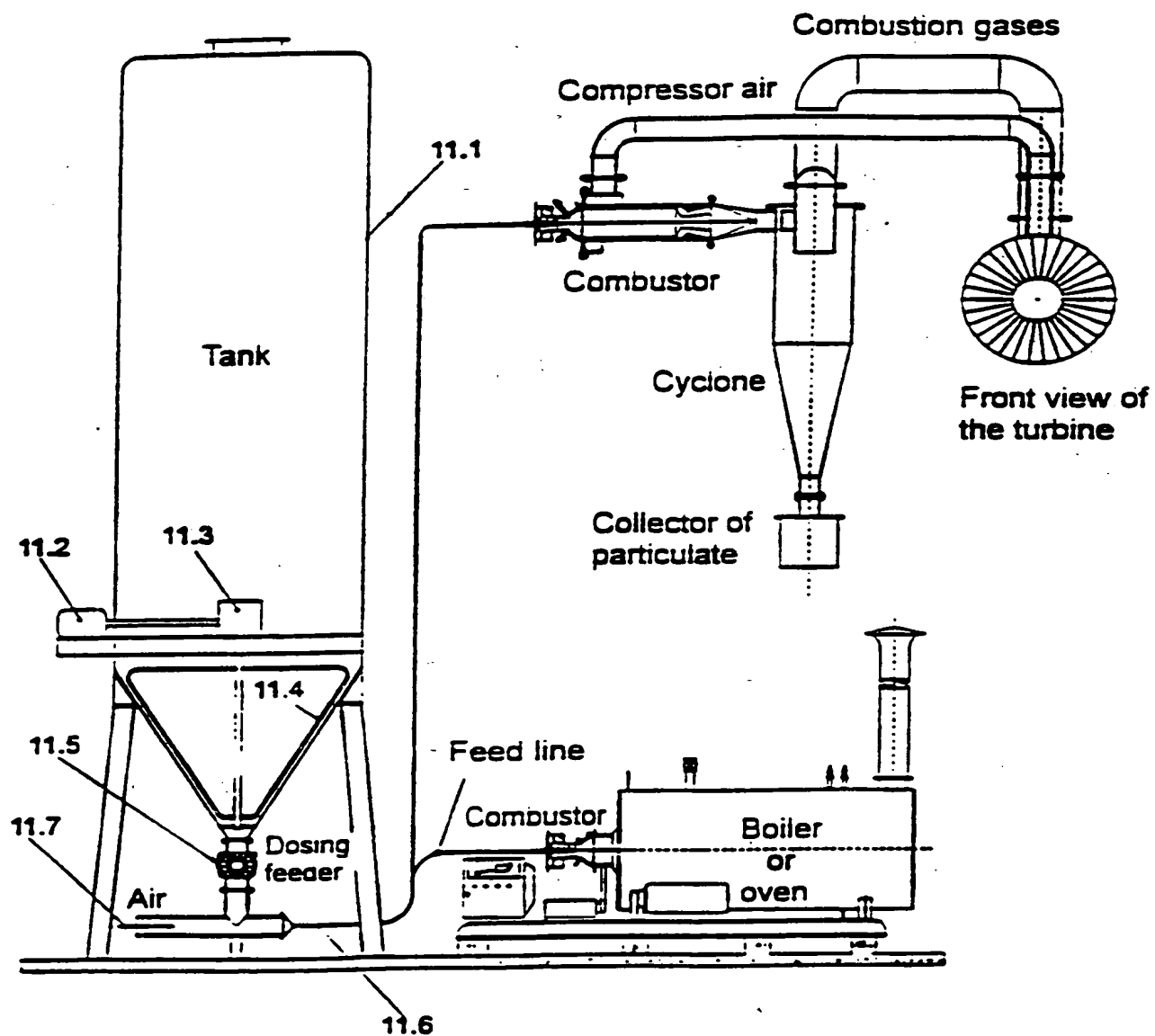
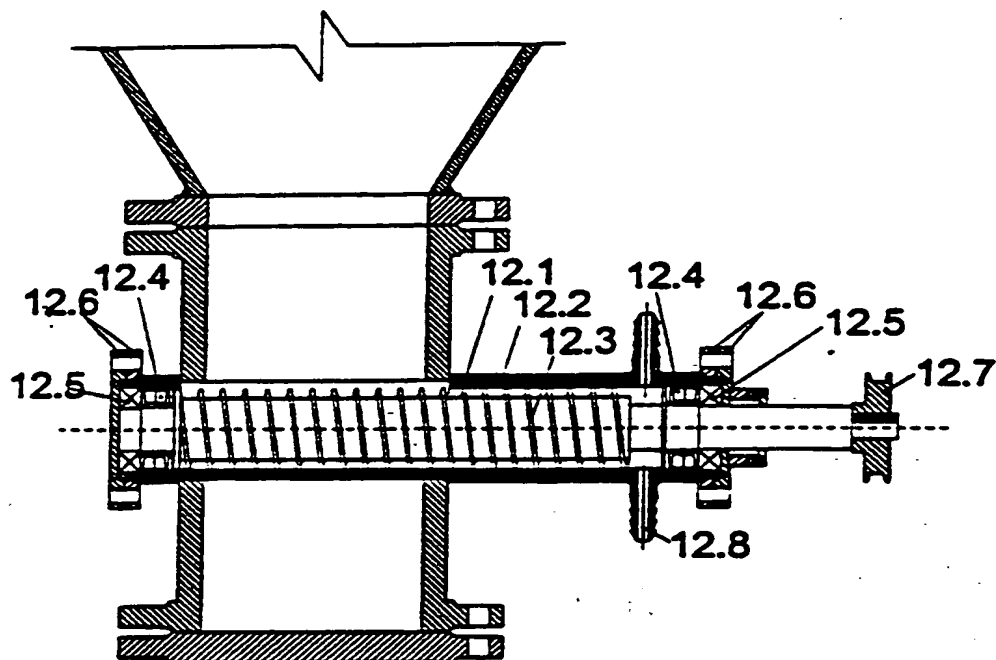
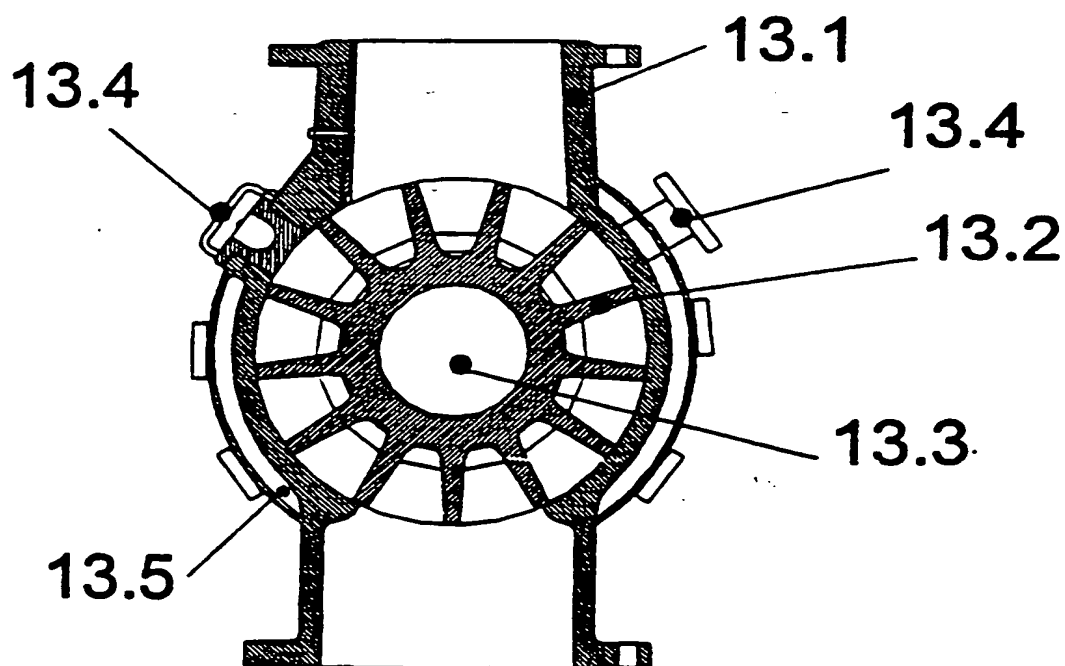


FIG 7b Average specific power irradiated in the combustion
a catalytic cellulignin particle (logarithmic scale)

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**FIG 8** Catalytic Cellulignin feeding system for Boilers/Ovens or gas turbines

9/11

**FIG 9** Helical feeder**FIG 10** Rotary valve

10/11

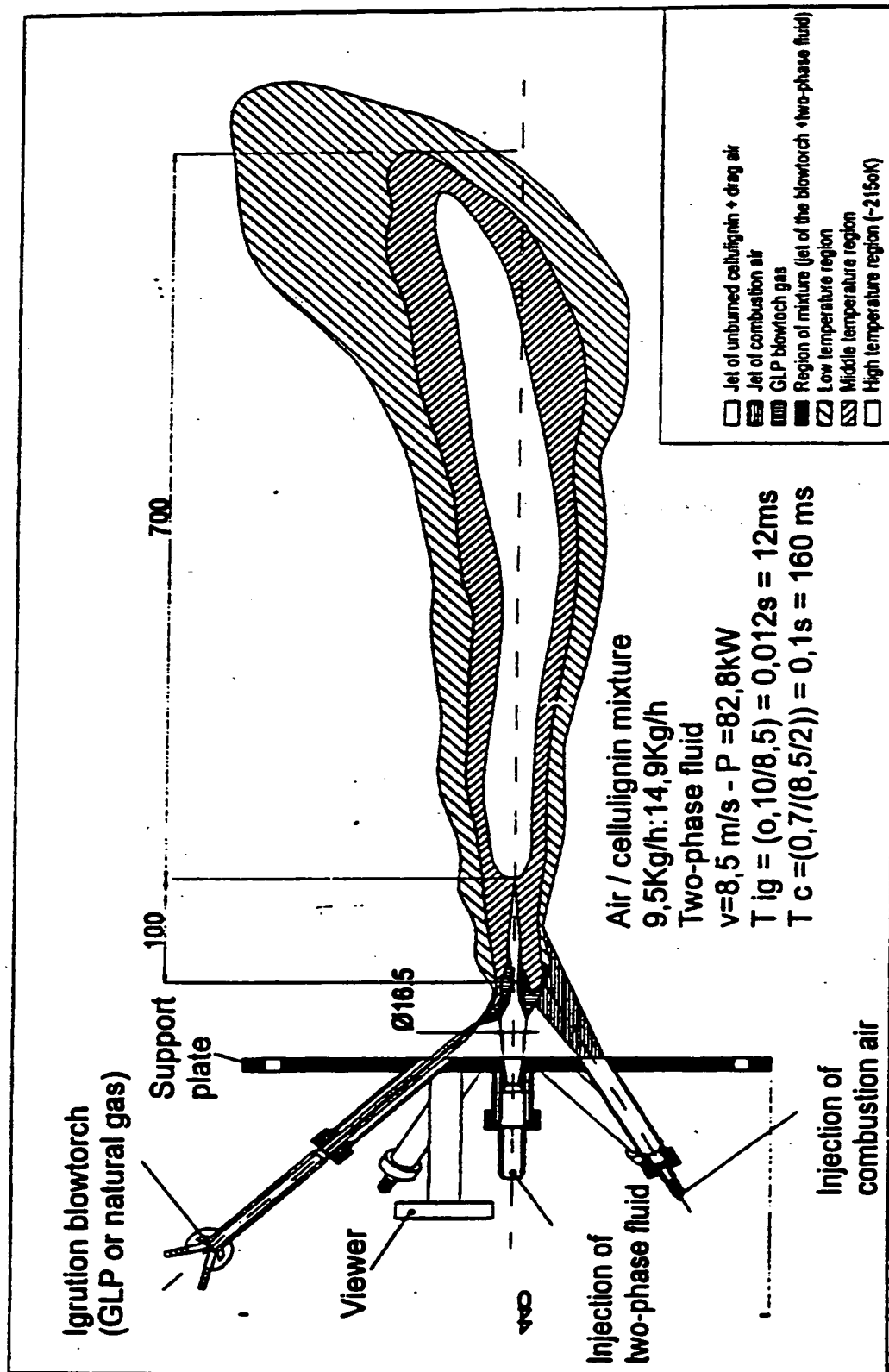


FIG 11 Axial combustor with flame of cellulignin in an open environment

11/11

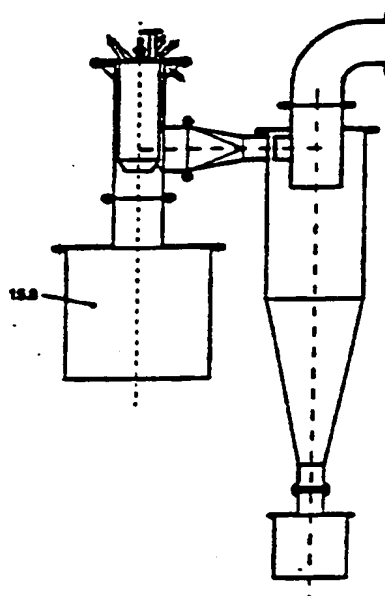


FIG 12a Combustor for cellulignin, cycloning and collection of particulates (horizontal)

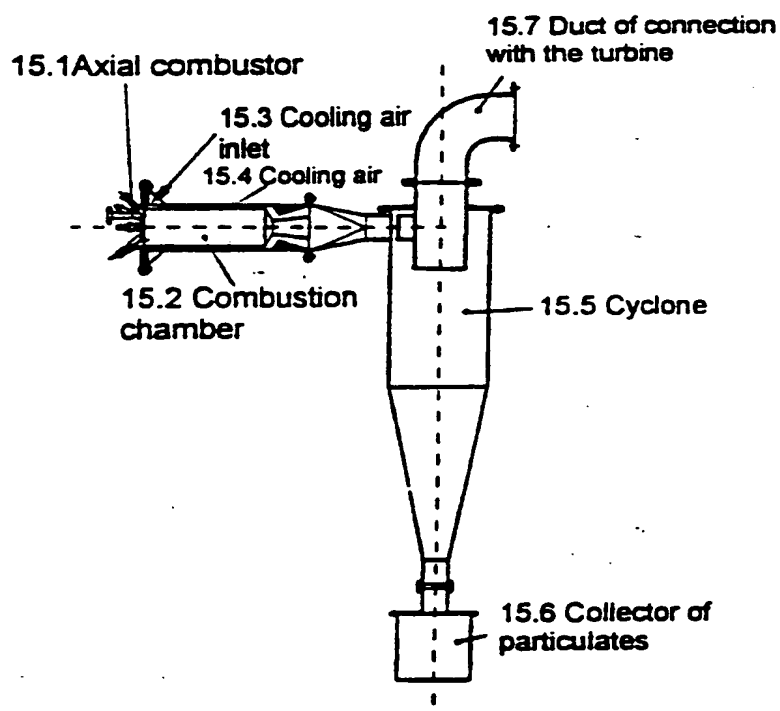


FIG 12b Combustor for cellulignin, cycloning and collection of particulates (vertical)

INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/BR 00/00066

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L5/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L C13K D21B D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US 5 338 366 A (GRACE TODD S ET AL) 16 August 1994 (1994-08-16) claims 1-29	1-8
X	GB 1 569 138 A (VALKANAS GEORGE N;KOUKIOS EMMANUEL G) 11 June 1980 (1980-06-11) page 2, line 18 -page 3, line 26	1-8
X	US 5 366 558 A (BRINK DAVID L) 22 November 1994 (1994-11-22) claim 1	1-8
X	EP 0 265 111 A (ICI PLC) 27 April 1988 (1988-04-27) the whole document	1-8

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

4 October 2000

Date of mailing of the international search report

13/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Zuurdeeg, B

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5338366 A	16-08-1994	BR 9305401 A	26-07-1994
GB 1569138 A	11-06-1980	AR 221819 A	31-03-1981
		AU 504082 B	04-10-1979
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		ES 2033319 T	16-03-1993
		FI 874605 A,B,	21-04-1988
		US 5340403 A	23-08-1994

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No. **00 / 0 0 0 6 6**

23 JUN 2000 23 - 6 - 00
International Filing Date

INTEL. BUREAU OF INTERNATIONAL APPLICATION
Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) **PE- 38 48**

Box No. I TITLE OF INVENTION
"CATALYTIC CELLULIGNIN FUEL"

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

RM MATERIAIS REFRAATÓRIOS LTDA.
Estrada do Pinhal, 750
12600-000 - Lorena - SP
Brazil

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State (that is, country) of nationality:

BR

State (that is, country) of residence:

BR

This person is applicant for the purposes of:

☐

all designated States

☒

all designated States except the United States of America

☐

the United States of America only

☐

the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

GARCIA PINATTI, DALTRO
Rua Oswaldo Aranha, 1194, casa 1,
Vila Zelía
Lorena, São Paulo
Brazil

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

BR

State (that is, country) of residence:

BR

This person is applicant for the purposes of:

☐

all designated States

☐

all designated States except the United States of America

☒

the United States of America only

☐

the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒

agent

☐

common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

DANNEMANN, SIEMSEN, BIGLER & IPANEMA MOREIRA
Caixa Postal 2142
Rua Marquês de Olinda, 70
Botafogo
22251-040 - Rio de Janeiro - RJ
Brazil

Telephone No.

(21) 553-1811

Facsimile No.

(21) 553-1812
553-1813

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>VIEIRA, CHRISTIAN ALEXANDRE Av. Andrade Neves, 710, apto. 33 Centro Campinas, São Paulo Brazil</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
<p>State (that is, country) of nationality: BR</p>	<p>State (that is, country) of residence: BR</p>
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>GUEDES SOARES, ALVARO Rua Madre Amanda de Castro Junqueira, 117 Mirante Mogi Mirim, São Paulo Brazil</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
<p>State (that is, country) of nationality: BR</p>	<p>State (that is, country) of residence: BR</p>
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
<p>State (that is, country) of nationality:</p>	<p>State (that is, country) of residence:</p>
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
<p>State (that is, country) of nationality:</p>	<p>State (that is, country) of residence:</p>
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☒ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|--|--|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MA Morocco |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> DM Dominica | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TZ United Republic of Tanzania |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> ZA South Africa |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | |
| <input checked="" type="checkbox"/> KR Republic of Korea | |
| <input checked="" type="checkbox"/> KZ Kazakhstan | |
| <input checked="" type="checkbox"/> LC Saint Lucia | |
| <input checked="" type="checkbox"/> LK Sri Lanka | |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

- ☐
- ☐

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claim(s) indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 23 June 1999 (23.06.99)	PI 9902606-6	BR		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

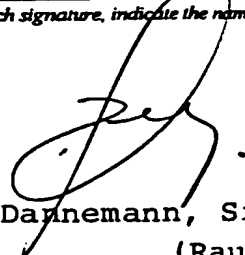
Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):	Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):		
ISA/ EPO	Date (day/month/year)	Number	Country (or regional Office)

Box No. VIII CHECK LIST: LANGUAGE OF FILING

<p>This international application contains the following number of sheets:</p> <p>request : 04</p> <p>description (excluding sequence listing part) : 36</p> <p>claims : 01</p> <p>abstract : 01</p> <p>drawings : 11</p> <p>sequence listing part of description : -</p> <p>Total number of sheets : 53</p>	<p>This international application is accompanied by the item(s) marked below:</p> <p>1. <input type="checkbox"/> fee calculation sheet</p> <p>2. <input type="checkbox"/> separate signed power of attorney</p> <p>3. <input type="checkbox"/> copy of general power of attorney; reference number, if any:</p> <p>4. <input type="checkbox"/> statement explaining lack of signature</p> <p>5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s):</p> <p>6. <input type="checkbox"/> translation of international application into (language):</p> <p>7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material</p> <p>8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form</p> <p>9. <input type="checkbox"/> other (specify):</p>
Figure of the drawings which should accompany the abstract: 7a	Language of filing of the international application: English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).



Darnemann, Siemsen, Bigler & Ipanema Moreira
(Raul Hey)

For receiving Office use only		<p>2. Drawings:</p> <p><input type="checkbox"/> received:</p> <p><input type="checkbox"/> not received:</p>
1. Date of actual receipt of the purported international application: 23 JUN 2000 23-6-00		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA/	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.	

PCT

FEE CALCULATION SHEET Annex to the Request

For receiving Office use only

International application No. 00 / 0 0 0 5 6

Applicant's or agent's
file reference

PE-3848

Date stamp of the receiving Office

Applicant

RM MATERIAIS REFRATÁRIOS LTDA. et al

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 236,00 T
2. SEARCH FEEDER . 462.07. x 0.876363 404,94 S

International search to be carried out by EPO

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

INTERNATIONAL FEE

Basic Fee

The international application contains 53 sheets.

first 30 sheets CHF 650 x 1.10502 718,26 b1

23 x CHF 15 x 1.10502 = 381,23 b2

remaining sheets additional amount

Add amounts entered at b1 and b2 and enter total at B 1.099,49 B

Designation Fees

The international application contains 83 designations.

8 x CHF 140 x 1.10502 = 1.237,62 D

number of designation fees payable (maximum 8) amount of designation fee

Add amounts entered at B and D and enter total at I 2.337,11 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) 75,00 P

5. TOTAL FEES PAYABLE R\$ 3.053,05

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☐ authorization to charge
deposit account (see below)

☐ cheque

☐ postal money order

☐ bank draft

☒ cash

☐ revenue stamps

☐ coupons

☐ other (specify):

DEPOSIT ACCOUNT AUTHORIZATION (this mode of payment may not be available at all receiving Offices)

The RO/ ☐ is hereby authorized to charge the total fees indicated above to my deposit account.

☐ (this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

Deposit Account No.

Date (day/month/year)

Signature

PATENT COOPERATION TREATY

SD
CP
ver agenda
10-12-00
13-12-00
#

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

DANNEMANN, SIEMSEN, BIGLER &
IPANEMA MOREIRA
Rua Marques de Olinda 70, Botafogo
Caixa Postal 2142
22251-040- Rio de Janeiro - RJ
BRAZIL

Date of mailing
(day/month/year)

13/10/2000

Applicant's or agent's file reference

PE-3848

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/BR 00/ 00066

International filing date
(day/month/year)

23/06/2000

Applicant

RM MATERIAIS REFRATARIOS LTDA.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

 European Patent Office, P.B. 5818 Patentlaan 2
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Fax: (+31-70) 340-3016

Authorized officer

Toñi Muñoz-Manneken

maria carmen

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

TENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PE-3848	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/BR 00/ 00066	International filing date (day/month/year) 23/06/2000	(Earliest) Priority Date (day/month/year) 23/06/1999
Applicant RM MATERIAIS REFRATARIOS LTDA.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/BR 00/00066

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L5/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L C13K D21B D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 338 366 A (GRACE TODD S ET AL) 16 August 1994 (1994-08-16) claims 1-29 ✓	1-8
X	GB 1 569 138 A (VALKANAS GEORGE N; KOUKIOS EMMANUEL G) 11 June 1980 (1980-06-11) page 2, line 18 - page 3, line 26 ✓	1-8
X	US 5 366 558 A (BRINK DAVID L) 22 November 1994 (1994-11-22) ✓ claim 1	1-8
X	EP 0 265 111 A (ICI PLC) 27 April 1988 (1988-04-27) ✓ the whole document	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

4 October 2000

Date of mailing of the international search report

13/10/2000

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Authorized officer

Zuurdeeg, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BR 00/00066

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5338366	A	16-08-1994	BR	9305401 A	26-07-1994
GB 1569138	A	11-06-1980	AR	221819 A	31-03-1981
			AU	504082 B	04-10-1979
			AU	1881076 A	27-04-1978
			BR	7607104 A	13-09-1977
			DE	2647910 A	05-05-1977
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			ES	452669 A	01-04-1978
			FR	2328795 A	20-05-1977
			IN	146710 A	18-08-1979
			IN	145513 A	28-10-1978
			IT	1076827 B	27-04-1985
			JP	52081103 A	07-07-1977
			PT	65746 A, B	01-11-1976
			ZA	7606073 A	28-09-1977
US 5366558	A	22-11-1994	US	4384897 A	24-05-1983
			US	4706903 A	17-11-1987
			US	5221357 A	22-06-1993
			US	5536325 A	16-07-1996
			US	5628830 A	13-05-1997
			AU	550028 B	27-02-1986
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			CA	1175820 A	09-10-1984
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			AU	611399 B	13-06-1991
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			BR	8705576 A	24-05-1988
			CA	1309403 A	27-10-1992
			DE	3777530 D	23-04-1992
			DK	549587 A	21-04-1988
			ES	2033319 T	16-03-1993
			FI	874605 A, B,	21-04-1988
			US	5340403 A	23-08-1994

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PCT - Chapter II

MU DG2

Att.: International Preliminary

Examining Authority

Examiner: Van Iddekinge, R

Rio, June 20, 2001

Fax.: 0049 89 2399 4465

Ref.: PCT - International Application PCT/BR00/00066

filed on June 23, 2000

RM MATERIAIS REFRAATÓRIOS LTDA.

Our ref.: PE-3848 (MCB)

Dear Sirs,

In response to the first written opinion issued on the above case, applicant respectfully submits that the present application meets both novelty and inventive requirements over the prior art references D1, D2, D3 and D4.

Claims 1 to 8 were rejected under the assumption that D1 to D4 would disclose the same process steps for treating biomass and that the resulting product of said processes would be identical to the cellulignin fuel defined in the present application. As it will be clarified below, the present invention is a cellulignin product comprising specific, distinct and unexpected characteristics which is obtained through a process involving different parameters when compared to the prior art.

Firstly it is noticed that a detailed description of the presently claimed solid cellulignin structure and its catalytic (fuel) characteristics is presented throughout the specification with reference to the illustrative drawings.

US Pat 5,338, 366 (D1) relates to a process of pre-hydrolysis of biomass which is described as a preliminary method for other techniques for treating biomass such as

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hydrolysis of cellulose, paper pulp production, alcohol and furfural production and others. It must be stressed the referred to patent describes the resulting solid in the form of a slurry containing the swollen biomass and does not make any mention of the obtention of a solid product that could present the same features as presently claimed nor the use of that solid as a fuel, which is the key point of the present invention.

A brief summary of the method proposed in the above US patent is presented below:

- mixing the biomass with a mineral acid (0.5 – 3% - 54 at 65°C) forming a slurry with a consistency that guarantees the biomass wetability by the acid in sufficient concentration (8 – 12% of solids) for eventually hydrolyzing the hemicellulose;
- dewatering of the slurry (35 – 50% of solids) in a screw press for minimizing the necessary amount of steam and maintaining the sugar concentration at reasonable levels in the following stages of the pre-hydrolysis;
- heating the dewatered slurry by directly contacting it with steam up to the reaction temperature and pressure; the pre-hydrolysis is carried in a tower-type vertical reactor (conventional) at a temperature of from 121 – 177° C, under the pressure of from 2.1 to 3.6 atm., for 2 – 40 minutes. This stage takes place at the top of the reactor with a consistency of 34% at the top and 24% at the bottom. In order to withdraw the solid/pre-hydrolysate mixture at the outlet of the reactor bottom, a dilution and cooling of the pre-hydrolysate until 8 – 12% of consistency and temperature of 82°C.
- retaining the biomass of the dewatered slurry in those temperature and pressure conditions for a time sufficient for the hemicellulose pre-hydrolysis.
- adding mineral acid to the liquid resulting from the dewatered from the screw press (pressate);
- heating the liqueur/acid mixture;
- using the liqueur/acid mixture as a source of acidic solution in stage (a);
- the liqueur/acid mixture is preheated up to 55° C (stage f) in an indirect heat exchanger that is heated by the final pre-hydrolysate resulting from the pre-hydrolysis stage.

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A fluffer may be used between the stages (b) and (c) for fluffing the biomass at the inlet of the tower-type vertical pre-hydrolysis reactor.

As can be seen from the above summary, the process steps described in reference D1 (US5,338,366) do not anticipate nor foresee the specific parameters now disclosed in the present application nor the final solid product thus obtained.

Patent GB Pat 1569238 (D2) relates to "an extremely light pre-hydrolysis" with acid contents lower than 1% and temperature lower than 160°C (reactor coated with Teflon). The object of that patent is the obtention of cellulose pulp with recovery of the monosaccharides generated by the decomposition of hemicellulose. In fact, since the main objective of GB Pat 1569138 is to obtain a cellulose pulp, the acidic process should be as mild as possible, so that there will not be any damage to the cellulose fiber, in order not to affect its mechanical strength.

According to the present invention, however, the object is exactly the opposite, that is to say, a pre-hydrolysis with intermediate amounts of sulfuric acid (1 - 2%) and at intermediate temperature range (160 - 170 °C) with the purpose of generating the macromolecular porosity to achieve a catalytic combustion (direct interaction of oxygen with carbon similar to natural gas). Consequently, the resulting product from the process claimed in D2 is distinct from the cellulignin according to the present application.

The following comparative text illustrates the two distinct kinds of hydrolysis. Only in the case of the present invention the process is carried out at intermediary conditions, which requires more simple reactors and parameters (batch processing, coating of the reactors with refractory metals (Ti, Nb, Ta and alloys thereof), average acid contents (1 - 2%), average temperatures (160 - 170°C), short times (20 - 30 minutes)):

GB Pat 1569138 (Total hydrolysis in 1st and 2nd stages) = Light pre-hydrolysis; obtention of pulp with cellulose fibers without fractures or pores; recovery of carbohydrates from the hemicelluloses; polysaccharides digestion; no worry about obtaining a solid with microstructure with macromolecular porosity.

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Present invention = Medium pre-hydrolysis; main objective: solid with microstructure with macromolecular porosity in the cellulignin; average contents of acid; average temperatures; short reaction time

Patent US 5366558 (D3) deals with the classic process of "total hydrolysis" in two steps aiming at the total decomposition of carbohydrates and according to which there is no worrying about the preservation of a solid material and much less worrying about creating a porous microstructure at macromolecular (catalytic) level therein (the solid is actually referred to "residue" – column 22 line 46). Therefore, this patent text clearly indicates that a solid product as claimed in the present application could not be obtained by that process.

The process disclosed in Pat. 5,366,558 presents the following characteristics in its first stage which are distinct from the process used to prepare the cellulignin of the present invention:

According to the above patent a continuous process is used wherein a significant complexity is required for the equipment and for the flows of liquids. In the present application, on the other hand, it is disclosed a batch process aiming at the simplicity of the equipment and of the flows of liquids. Due to its enormous complexity, the equipment described in Pat 5,366,558 can only be manufactured from stainless steel or nickel alloys (column 9 line 56), for which reason acidic solutions with pH between 2.0 and 3.0 (column 1 line 35) are used. Solutions with lower pH (~ 1) would cause serious corrosions.

The drawbacks of the pre-hydrolysis (1st stage) of Pat 5,366,558 due to the above-mentioned factors makes it necessary to produce large surfaces for implementing the processes of the second stage by a disintegrator (column 3 line 60), to eliminate the deficiencies of the first stage. Although Pat 5,366,558 does not contain any quantitative information on the granulometry achieved in the disintegrator, it generates macroscopic particles having surfaces considerably larger than the surface generated by the macromolecular porosity (catalytic) obtained according to the present invention.

In summary, Pat 5,366,558 does not provide for equipments (materials), processes and characterization of the cellulignin microstructure after the first stage because its objective is the total disintegration of the solid in the subsequent stage. In

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present invention, on the other hand, the pre-hydrolysis (first stage) process was extended to obtain a microstructure with macromolecular porosity for achieving a catalytic combustion, said microstructure being not described nor foreseen in the above mentioned prior art reference.

EP Pat 0265111 A2 (D4) relates to the xylose production from the liquid portion of hydrolysis processes. This patent claims a processing the hydrolyzed liquid fraction of biomass. Again the product resulting from that patented process has clearly nothing to do with the solid catalytic cellulignin claimed in the present invention.

In fact, EP Pat 0265111 refers to the solid portion as an "insoluble residue", which is disposed of. There is no further consideration (technology) regarding the "solid residue". The fact that the solid portion is considered only as a residue in this patent as well as in most of earlier prior art patents relating to pre-hydrolysis process is the reason why up to the present invention there had been no optimization of the process conditions and parameters with the purpose of obtaining a fuel with the now claimed specific characteristics.

In present case, the inventors have taken a diametrically opposed way, that is to say, they have achieved improved conditions for the pre-hydrolysis process which allowed the obtention of a solid product with macromolecular porosity characteristics typical of a catalytic fuel. In other words, according to the present invention, the parameters such as time, temperature, acidic contents, stirring, hydric module (liquid contents/solid contents ratio) were optimized in order to yield a new and different resulting product that is composed of cellulose and globulized cellulignin with the specific surface of about 1.5 to 2.5 m²/g.

The resulting cellulignin according to the present invention is porous at macromolecular level, demineralized, friable, able to be ground down to submetric particles with low consumption of energy, easily dryable with the residual heat from the combustion gases at 230° C in short periods of time simultaneously with the grinding. These characteristics are a result of the

In view of the clarifications presented above, applicant respectfully submits that the invention as now claimed is novel and inventive over the prior art represented by D1 to D4.

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Finally it is also observed that the expression "celluliginin fuel" is indeed the most appropriate technical expression to identify the claimed product and as far as the applicant is aware, it will be promptly understood by any person skilled in the art. For this reason, no amendment was effected therein.

Very truly yours


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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

19 OCT 06 13 01

Valued at: 100,000
BILDER & L. MOREIRA

Date of mailing
(day/month/year)

02.10.2001

Applicant's or agent's file reference
PE-3848

IMPORTANT NOTIFICATION

International application No.
PCT/BR00/00066

International filing date (day/month/year)
23/06/2000

Priority date (day/month/year)
23/06/1999

Applicant

RM MATERIAIS REFRATARIOS LTDA.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference PE-3848	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/BR00/00066	International filing date (day/month/year) 23/06/2000	Priority date (day/month/year) 23/06/1999
International Patent Classification (IPC) or national classification and IPC C10L5/44		
Applicant RM MATERIAIS REFRATARIOS LTDA.		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.
 - ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 22/01/2001	Date of completion of this report 02.10.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Van Iddekinge, R Telephone No. +49 89 2399 8346 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/BR00/00066

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-36 as originally filed

Claims, No.:

1-8 as originally filed

Drawings, sheets:

1-11 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/BR00/00066

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1-8
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-8
Industrial applicability (IA)	Yes:	Claims 1-8
	No:	Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- 1). Reference is made to the following documents:

D1=US-A-5338366

D2=GB-A-1569138

D3=US-A-5366558

D4=EP-A-265111

D5=Bioresource Technology, vol. 59 (1997), pages 129-136

- 2). According to the present application the claimed fuel is prepared by treating biomass with an acidic solution under influence of heat and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see page 11, line 18 - page 12, line 5. The biomass can be any type of biomass such as wood, sugar cane bagasse, straw, vegetable residues, barks, grass, etc.

- D1 describes treating biomass (sugar cane bagasse) with an acidic solution (mineral acid 0.5-3.0%) under influence of heat (250-350°F) and pressure (30-50 psig) until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see claims 28, 29. The residue corresponds to the presently claimed catalytic cellulignin fuel.

- D2 describes treating cellulosic agricultural by-products (alfalfa, wheat straw, rice straw) with an acidic solution (mineral acid 0.1-1.0%) under influence of heat (100-160°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see page 2, lines 42-57; page 6, lines 28-33; claims 1, 4-6, 8, 18. The residue corresponds to the presently claimed catalytic cellulignin fuel.

- D4 describes treating lignocellulosic feedstocks (straw) with an acidic solution (mineral acid 0.5-5.0%) under influence of heat (100-150°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see claims 1, 4-6. The residue corresponds to the presently claimed catalytic cellulignin fuel.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/BR00/00066

- D5 describes treating lignocellulosic feedstocks (i.e. corn stover, poplar and switchgrass) with an acidic solution (sulfuric acid 0.6, 0.9 and 1.2 wt.%) under influence of heat (140, 160, 180°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see D5: page 129, "Abstract"; pages 130-131, "METHODS".

Since D1, D2, D4 and D5 disclose the same process steps, the resulting product should be identical. Thus D1, D2, D4 and D5 disclose a fuel according to claims 1-8 of the application.

Therefore claim 1 and its dependent claims 2-8 do not fulfil the requirements of Article 33(2) PCT (novelty).

Re Item VII

Certain defects in the international application

- 3). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1, D2 and D5 is not mentioned in the description, nor are these documents identified therein.

Re Item VIII

Certain observations on the international application

- 4). The term "catalytic cellulignin fuel" used in claims 1-8 is vague and unclear and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).

PATENT COOPERATION TREATY

ver agenda
31-4-2001
31-5-2001
1-6-2001
21-6-2001

DANNEMANN, SIEMSEN & CO. PATENT ANWALTE

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DANNEMANN, SIEMSEN, BIGLER &
IPANEMA MOREIRA
Rua Marques de Olinda 70, Botafogo
Caixa Postal 2142
22251-040- Rio de Janeiro - RJ
BRESIL

PCT

WRITTEN OPINION

(PCT Rule 66)

28 MAR 09 22 2001

Date of mailing (day/month/year)		21.03.2001
Applicant's or agent's file reference PE-3848		REPLY DUE within 3 month(s) from the above date of mailing
International application No. PCT/BR00/00066	International filing date (day/month/year) 23/06/2000	Priority date (day/month/year) 23/06/1999
International Patent Classification (IPC) or both national classification and IPC C10L5/44		
Applicant RM MATERIAIS REFRATARIOS LTDA.		


- This written opinion is the first drawn up by this International Preliminary Examining Authority.
- This opinion contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain document cited
 - VII ☒ Certain defects in the international application
 - VIII ☒ Certain observations on the international application
- The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.
- The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 23/10/2001.

Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer / Examiner Van Iddekinge, R
	Formalities officer (incl. extension of time limits) Christensen, J Telephone No. +49 89 2399 8052



Handwritten signature

WRITTEN OPINION

International application No. PCT/BR00/00066

I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*):

Description, pages:

1-36 as originally filed

Claims, No.:

1-8 as originally filed

Drawings, sheets:

1-11 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

WRITTEN OPINION

International application No. PCT/BR00/00066

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement
- | | | |
|-------------------------------|--------|-----|
| Novelty (N) | Claims | 1-8 |
| Inventive step (IS) | Claims | 1-8 |
| Industrial applicability (IA) | Claims | |

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**WRITTEN OPINION
SEPARATE SHEET**

International application No. PCT/BR00/00066

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- 1). Reference is made to the following documents:

D1=US-A-5338366
D2=GB-A-1569138
D3=US-A-5366558
D4=EP-A-265111

- 2). According to the present application the claimed fuel is prepared by treating biomass with an acidic solution under influence of heat and pressure until the hemicellulose is converted into sugar and then removing the sugar (by means of washing), see page 11, line 18 - page 12, line 5.

Since D1, D2, D3 and D4 disclose the same process steps, the resulting product should be identical, see D1: column 5, lines 27-39; claims 27-29 and D2: claim 1 and D3: claim 1 and D4: claim 1; page 2, line 41-page 3, line 4.

Therefore claim 1 and its dependent claims 2-8 do not fulfil the requirements of Article 33(2) PCT (novelty).

If the applicant does not agree with the novelty objection, the applicant should indicate in the letter of reply the difference of the subject-matter of the claims vis-à-vis the state of the art (product features of the claims not disclosed in the prior art) and the significance thereof for the inventive step. //

Re Item VII

Certain defects in the international application

- 3). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.

**WRITTEN OPINION
SEPARATE SHEET**

International application No. PCT/BR00/00066

Re Item VIII

Certain observations on the international application

- 4). The term "catalytic cellulignin fuel" used in claims 1-8 is vague and unclear and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).

The demand must be filed directly with the competent International Preliminary Examining Authority. If two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ EPO

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA		Date of receipt of DEMAND	
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference PE- 38 48	
International application No. PCT/BR00/00066	International filing date (day/month/year) 23 June 2000 (23.06.2000)	(Earliest) Priority date (day/month/year) 23 June 1999 (23.06.99)	
Title of invention "CATALYTIC CELLULIGNIN FUEL"			
Box No. II APPLICANT(S)			
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) RM MATERIAIS REFRAATÓRIOS LTDA. Estrada do Pinhal, 750 12600-000 - Lorena - SP Brazil		Telephone No.: Facsimile No.: Teleprinter No.:	
State (that is, country) of nationality: BR		State (that is, country) of residence: BR	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) GARCIA PINATTI, DALTRO Rua Oswaldo Aranha, 1194 - casa 1 Vila Zelia Lorena, São Paulo Brazil			
State (that is, country) of nationality: BR		State (that is, country) of residence: BR	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) VIEIRA, CHRISTIAN ALEXANDRE Av. Andrade Neves, 710, apto. 33 Centro Campinas, São Paulo Brazil			
State (that is, country) of nationality: BR		State (that is, country) of residence: BR	
<input checked="" type="checkbox"/> Further applicants are indicated on a continuation sheet.			

Continuation of Box No. II APPLICANT(S)

If none of the following sub-boxes is used, this sheet should not be included in the demand.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

GUEDES SOARES, ALVARO
Rua Madre Amanda de Castro Junqueira, 117
Mirante
Mogi Mirim, São Paulo
Brazil

State *(that is, country)* of nationality:

BR

State *(that is, country)* of residence:

BR

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

☐ Further applicants are indicated on another continuation sheet.

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCEThe following person is ☒ agent ☐ common representativeand ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*DANNEMANN, SIEMSEN, BIGLER & IPANEMA MOREIRA
Caixa Postal 2142
Rua Marquês de Olinda, 70
Botafogo
22251-040 - Rio de Janeiro - RJ
Brazil

Telephone No.:

(5521) 553.1811

Facsimile No.:

(5521) 553.1812
553.1813

Teleprinter No.:

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.**Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION****Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filedthe description ☒ as originally filed☐ as amended under Article 34the claims ☒ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☐ as amended under Article 34the drawings ☒ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English☒ which is the language in which the international application was filed.☐ which is the language of a translation furnished for the purposes of international search.☐ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.**Box No. V ELECTION OF STATES**The applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes not to elect:

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | |
|--|---|--------|
| 1. translation of international application | : | sheets |
| 2. amendments under Article 34 | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | sheets |
| 5. letter | : | sheets |
| 6. other (specify) | : | sheets |

For International Preliminary Examining Authority use only

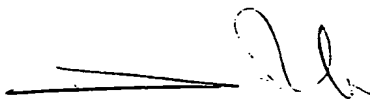
received	not received
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>

The demand is also accompanied by the item(s) marked below:

- | | |
|--|---|
| 1. <input checked="" type="checkbox"/> fee calculation sheet | 4. <input type="checkbox"/> statement explaining lack of signature |
| 2. <input type="checkbox"/> separate signed power of attorney | 5. <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form |
| 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: | 6. <input type="checkbox"/> other (specify): |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).



Dannemann, Siemsen, Bigler & Ipanema Moreira

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

PCT

FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

International application No. PCT/BR00/00066 <hr/> Applicant's or agent's file reference PE-3848 <hr/> Applicant RM MATERIAIS REFRATÁRIOS LTDA. <hr/> Calculation of prescribed fees 1. Preliminary examination fee DEM 749,58 P 2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>) DEM 287.51 H 3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box DEM 1.037.09 <div style="border: 1px solid black; width: 100px; margin-left: 100px; text-align: center;">TOTAL</div>	For International Preliminary Examining Authority use only <hr/> Date stamp of the IPEA <div style="border: 1px solid black; height: 150px; width: 100%;"></div>	
Mode of Payment <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <input type="checkbox"/> authorization to charge deposit account with the IPEA (see below) <input type="checkbox"/> cheque <input type="checkbox"/> postal money order <input checked="" type="checkbox"/> bank draft </div> <div style="width: 45%;"> <input type="checkbox"/> cash <input type="checkbox"/> revenue stamps <input type="checkbox"/> coupons <input type="checkbox"/> other (specify): </div> </div>		
Deposit Account Authorization (<i>this mode of payment may not be available at all IPEAs</i>) The IPEA/ _____ <input type="checkbox"/> is hereby authorized to charge the total fees indicated above to my deposit account. <input type="checkbox"/> (<i>this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit</i>) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.		
Deposit Account Number	Date (day/month/year)	Signature

PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DANNEMANN, SIEMSEN, BIGLER &
IPANEMA MOREIRA
Rua Marques de Olinda 70, Botafogo
Caixa Postal 2142
22251-040- Rio de Janeiro - RJ
BRESIL

non agenda
10-8-01
3-9-01
10-9-01

PCT

WRITTEN OPINION

(PCT Rule 66)

DANNEMANN, SIEMSEN, BIGLER & IPANEMA MOREIRA

Date of mailing
(day/month/year)

10.07.2001

Applicant's or agent's file reference

PE-3848

REPLY DUE

within 2 month(s)
from the above date of mailing

International application No.

PCT/BR00/00066

International filing date (day/month/year)

23/06/2000

Priority date (day/month/year)

23/06/1999

International Patent Classification (IPC) or both national classification and IPC

C10L5/44

Applicant

RM MATERIAIS REFRATARIOS LTDA.

1. This written opinion is the **second** drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain document cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 23/10/2001.

Name and mailing address of the international preliminary examining authority:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer / Examiner

Van Iddekinge, R

Formalities officer (incl. extension of time limits)

Gregoire, J-P

Telephone No. +49 89 2399 8041



maria carmen

I. Basis of the opinion

1. With regard to the **elements** of the international application (Replacement *sheets which have been furnished to the receiving Office in response to an invitation under Article 14* are referred to in this opinion as "*originally filed*");

Description, pages:

1-36 as originally filed

Claims, No.:

1-8 as originally filed

Drawings, sheets:

1-11 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

WRITTEN OPINION

International application No. PCT/BR00/00066

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N) Claims 1-8

Inventive step (IS) Claims 1-8

Industrial applicability (IA) Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- 1). According to the applicant (letter of 20.06.2001) the claimed catalytic cellulignin fuel product is novel because D1, D2, D3 and D4 disclose a different production process.
- 2). According to the present application the claimed fuel is prepared by treating biomass with an acidic solution under influence of heat and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see page 11, line 18 - page 12, line 5. The biomass can be any type of biomass such as wood, sugar cane bagasse, straw, vegetable residues, barks, grass, etc.

In D1 sugar cane bagasse is treated with an acidic solution (mineral acid 0.5-3.0%) under influence of heat (250-350°F) and pressure (30-50 psig) until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see claims 28, 29. The residue corresponds to the presently claimed catalytic cellulignin fuel.

In D2 straw is treated with an acidic solution (mineral acid 0.1-1.0%) under influence of heat (100-160°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see page 2, lines 42-57; page 6, lines 28-33; claims 1, 4-6, 8, 18. The residue corresponds to the presently claimed catalytic cellulignin fuel.

In D4 straw is treated with an acidic solution (mineral acid 0.5-5.0%) under influence of heat (100-150°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see claims 1, 4-6. The residue corresponds to the presently claimed catalytic cellulignin fuel.

Thus the novelty objection in view of D1, D2 and D4 is maintained.

Therefore claim 1 and its dependent claims 2-8 do not fulfil the requirements of Article 33(2) PCT (novelty).

If the applicant does not agree with the novelty objection, the applicant should indicate in the letter of reply the difference of the subject-matter of the claims vis-à-vis the state of the art (product features of the claims not disclosed in the prior art) and the significance thereof for the inventive step.

It is to be noted that D5 (Bioresource Technology, vol. 59 (1997), pages 129-136) also discloses the presently claimed catalytic cellulignin fuel.

Re Item VII

Certain defects in the international application

- 3). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.

Re Item VIII

Certain observations on the international application

- 4). The term "catalytic cellulignin fuel" used in claims 1-8 is vague and unclear and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).

If the applicant is of the opinion that the term "catalytic cellulignin fuel" used in claims 1-8 is well known and clear, the applicant should prove this by sending a copy of a document (or book) giving a definition of this term.

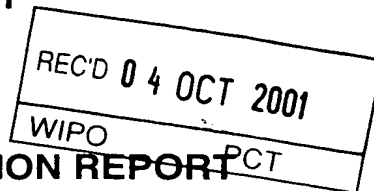
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)





Applicant's or agent's file reference PE-3848	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/BR00/00066	International filing date (day/month/year) 23/06/2000	Priority date (day/month/year) 23/06/1999
International Patent Classification (IPC) or national classification and IPC C10L5/44		
Applicant RM MATERIAIS REFRATARIOS LTDA.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
 - ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 22/01/2001	Date of completion of this report 02.10.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Van Iddekinge, R Telephone No. +49 89 2399 8346 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/BR00/00066

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-36 as originally filed

Claims, No.:

1-8 as originally filed

Drawings, sheets:

1-11 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/BR00/00066

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-8
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-8
Industrial applicability (IA)	Yes:	Claims	1-8
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- 1). Reference is made to the following documents:
D1=US-A-5338366
D2=GB-A-1569138
D3=US-A-5366558
D4=EP-A-265111
D5=Bioresource Technology, vol. 59 (1997), pages 129-136
- 2). According to the present application the claimed fuel is prepared by treating biomass with an acidic solution under influence of heat and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see page 11, line 18 - page 12, line 5. The biomass can be any type of biomass such as wood, sugar cane bagasse, straw, vegetable residues, barks, grass, etc.
 - D1 describes treating biomass (sugar cane bagasse) with an acidic solution (mineral acid 0.5-3.0%) under influence of heat (250-350°F) and pressure (30-50 psig) until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see claims 28, 29. The residue corresponds to the presently claimed catalytic cellulignin fuel.
 - D2 describes treating cellulosic agricultural by-products (alfalfa, wheat straw, rice straw) with an acidic solution (mineral acid 0.1-1.0%) under influence of heat (100-160°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see page 2, lines 42-57; page 6, lines 28-33; claims 1, 4-6, 8, 18. The residue corresponds to the presently claimed catalytic cellulignin fuel.
 - D4 describes treating lignocellulosic feedstocks (straw) with an acidic solution (mineral acid 0.5-5.0%) under influence of heat (100-150°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see claims 1, 4-6. The residue corresponds to the presently claimed catalytic cellulignin fuel.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/BR00/00066

- D5 describes treating lignocellulosic feedstocks (i.e. corn stover, poplar and switchgrass) with an acidic solution (sulfuric acid 0.6, 0.9 and 1.2 wt.%) under influence of heat (140, 160, 180°C) and pressure until the hemicellulose is converted into sugar (pre-hydrolysis of biomass) and then removing the sugar (by means of washing), see D5: page 129, "Abstract"; pages 130-131, "METHODS".

Since D1, D2, D4 and D5 disclose the same process steps, the resulting product should be identical. Thus D1, D2, D4 and D5 disclose a fuel according to claims 1-8 of the application.

Therefore claim 1 and its dependent claims 2-8 do not fulfil the requirements of Article 33(2) PCT (novelty).

Re Item VII

Certain defects in the international application

- 3). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1, D2 and D5 is not mentioned in the description, nor are these documents identified therein.

Re Item VIII

Certain observations on the international application

- 4). The term "catalytic cellulignin fuel" used in claims 1-8 is vague and unclear and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).